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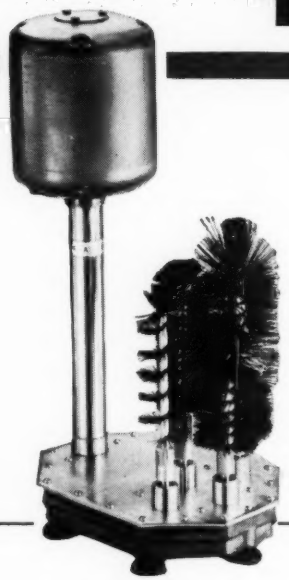

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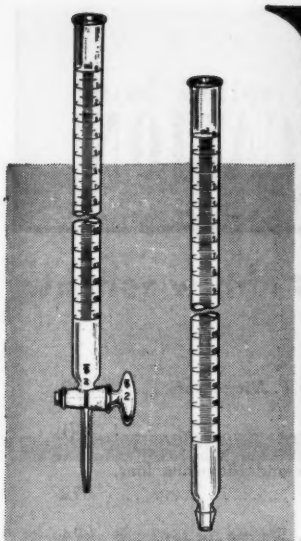

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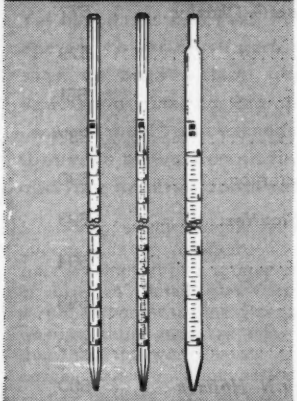

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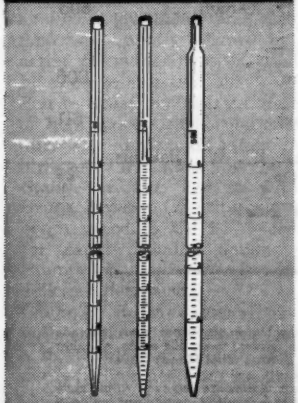

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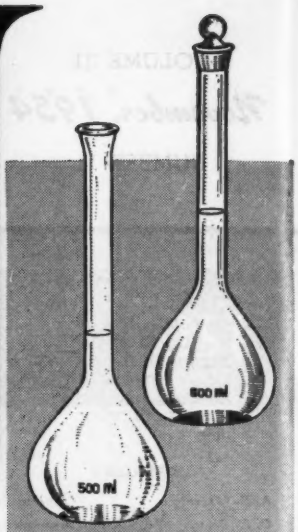

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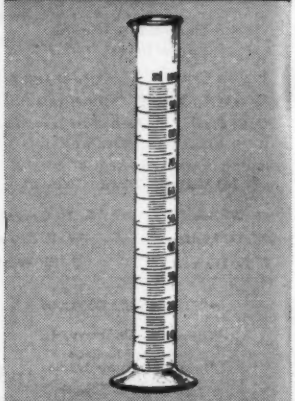

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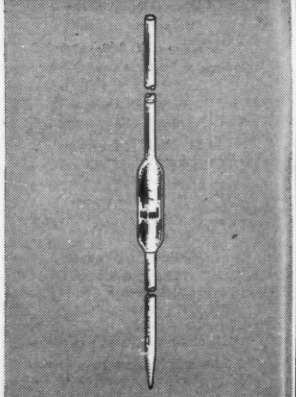

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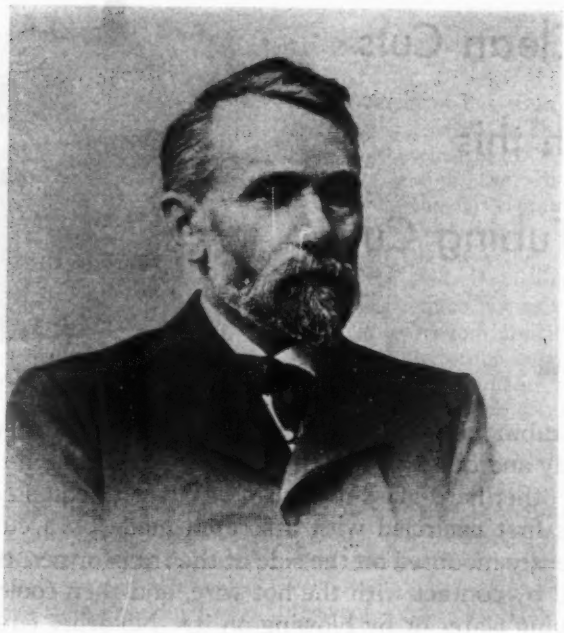

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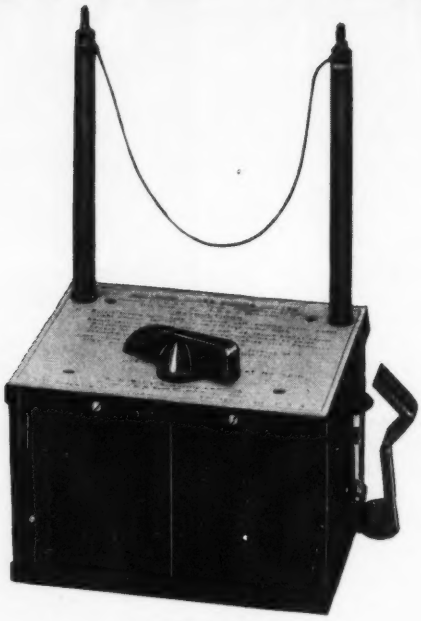

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Editor's Outlook

WE AMERICANS have not been generally known for our modesty. Everything which comes out of this country is supposed to be of the bigger-and-better variety. Only the Russians—our faithful imitators—can do a better job of this sort of boasting.

But when evaluating our productivity in pure science we have seldom done ourselves even fair justice. Whether we have been sold this idea by our friends and enemies or have conceived it independently, I do not know, but we have got into the habit of thinking that other people get the bright original ideas and we come along and make money by putting these ideas to work. To a certain extent this may be true, but if so it is the result of circumstances and events rather than any deficiency in the training or ability of our scientists and technicians.

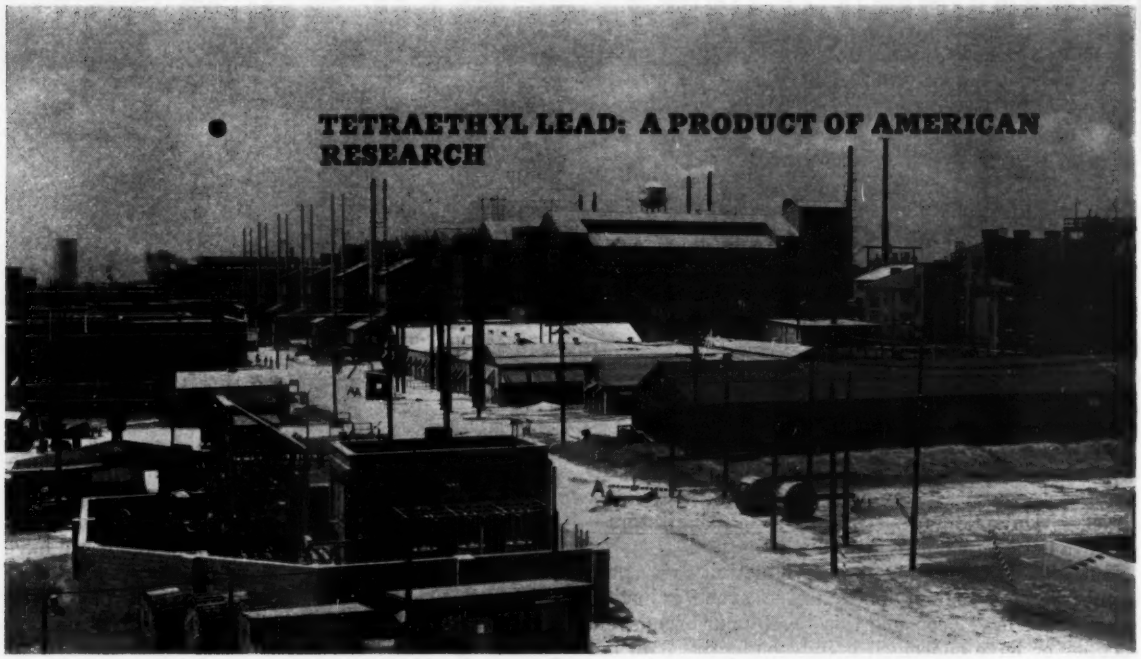
This sort of inferiority complex is not good for us and, things being as they are in the world today, what is not good for us is not good for the rest of the world either. As a matter of fact, American pure science has plenty of eminent examples: Benjamin Franklin, Count Rumford, Joseph Henry, Henry Rowland, Willard Gibbs, Michelson and Morley, Gilbert Lewis, Irving Langmuir, to mention only a few eminent figures in physical science. While no naturally occurring element has been discovered in this country, Americans have filled all the gaps in the periodic table and added a half-dozen synthetic transuranium elements. And several fields of pure science are now dominated by American workers.

The lead article in this issue describes the technical development of an American idea in pure science which has had far-reaching results. It has not only kept engines from knocking throughout the world but has led to fundamental knowledge about the structure of fuel substances and its relation to their combustion characteristics. It has even resulted in commercial methods for the production of two elements from sea water—bromine and magnesium.

Our country has always been glamorous for its spirit of *pioneering*. The romance of America has been in the clearing of the wilderness, the expanding of the frontiers, the adventure into the unknown. Because all this has required vigor and action we have come to be known as a nation of *doers* rather than thinkers. On the whole, this has been to our credit, but it must not be overlooked that adventure and pioneering require not only a bodily vigor and courage but also a freedom and independence of mind which are indeed the prime moving force of all adventurers. And now, in a world in which few physical frontiers remain and in which security and freedom from risk are being legislated from cradle to grave, the pioneering spirit must turn to intellectual wildernesses for adventure. And we are learning that this kind of adventure can be as exciting as any.

If our pure scientists have suffered by comparison with their brethren in the field of application and development it is because of lack of the proper encouragement. And this is the result of the economics of the situation, attracting a large proportion of the best minds into technology and development. Other highly industrialized nations—Britain, for example—also bewail the scarcity of fundamental research in pure science.

While our own condition of balance between pure and applied science is perhaps improving, it is far from satisfactory. Troubles of other nations in this regard can at least give us no joy. It all brings us back to the realization of certain urgent necessities: more students to choose science for a life career; more and better science teachers to inspire and train these students at every educational level; and appreciation on the part of the general public that this *is* necessary and deserving of adequate support. If we do not fill these three needs adequately, then we may indeed worry about the future of American pure science. And when *that* worry becomes acute a number of other, more painful ones will assuredly follow.



The Six Tetraethyl Lead Buildings at Ethyl Corporation's Baton Rouge Plant

STANTON P. NICKERSON
New York City, N. Y.

THIRTY-ONE years ago—on February 2, 1923—the first gallon of gasoline improved by tetraethyl lead was sold to a venturesome motorist in Dayton, Ohio. Since that time, over 525 billion gallons of leaded gasoline have been marketed in the United States, with the result that the manufacture of tetraethyl lead has become one of the ten largest industrial chemical enterprises in the nation.

The discovery of what tetraethyl lead can do to improve gasolines is a direct contribution of industrial research. The successful manufacture, utilization, and sale of antiknock compounds containing tetraethyl lead are achievements shared by several different companies. It is not generally realized nor appreciated, however, that a number of colleges and universities played an important part in the discovery, development, and application of this highly useful product, either by work conducted in university laboratories or by the active assistance of faculty members called in to help on specific problems.

Few industries, in fact, have an historical tap-root more deeply imbedded in the university laboratory, nor are many other industries more aware of their debt to pure and applied academic research. Tetraethyl lead might never have appeared on the market—at least when it did—without such cooperative assistance. The entire industry is a significant example of what can be accomplished by the close integration of academic and industrial research efforts.

To investigations conducted at Clark University, for example, the industry is indebted for the basic chemical manufacturing process it uses today. A clue developed at the Massachusetts Institute of Technology touched off a chain of thought which helped bring about the discovery of the antiknock properties of tetraethyl lead. M. I. T. research also contributed to an early understanding of fundamental problems associated with fuel knock.

From institutions like Harvard, Yale, Cornell, Johns Hopkins, Vanderbilt, Ohio State, and the Universities of Chicago, Cincinnati, Kansas, Virginia, and Wisconsin the new industry obtained personnel, inspiration, guidance, cooperation, and a variety of intangible as well as finite building blocks for the industrial structure as it now stands.

An understanding of the importance of such an historical root in educational institutions can be gained by a brief summary of what tetraethyl lead means to motorized transportation. The chemical compound plus certain other ingredients, when added to gasoline, controls the combustion of the air-fuel mixture in internal combustion engines, so that the fuel burns

smoothly and evenly when ignited. Before tetraethyl lead was commonly used, part of the air-fuel mixture had a tendency to detonate or explode. The detonation was heard as a knock or ping, and resulted in overheating, loss of power, and sometimes damage to the engine.

Development of the modern and efficient high-compression engine has been largely dependent upon the availability of high-quality gasolines. The discovery that tetraethyl lead is the most economical way to achieve this quality has been described as one of the most significant contributions to oil and automotive progress. The general use of tetraethyl lead has therefore played an important part in many of the advancements which have been made in the nation's entire system of motorized transportation.

It should be a source of satisfaction to all those interested in the technological and industrial history of the United States to realize that aside from a few remote developments, like the first laboratory production of tetraethyl lead in Germany a century ago, the entire industry is obligated to no other country for its origin and growth. The discovery of the product's use, its development as a gasoline additive, its manufacturing processes, the expansion of the business, and its contribution to better motorized transportation all stem from American ingenuity, initiative, and drive.

A large and complex undertaking like the tetraethyl lead industry has its beginnings in the efforts of a number of men. The first to undertake a full exploration of knock—its cause and its cure—was Charles F. Kettering of General Motors, who directed the work of the late Thomas Midgley, Jr., T. A. Boyd, and others associated with them. They discovered the antiknock properties of tetraethyl lead in the Research Laboratories of General Motors at Dayton on December 9, 1921, after five years of failure and disappointment.

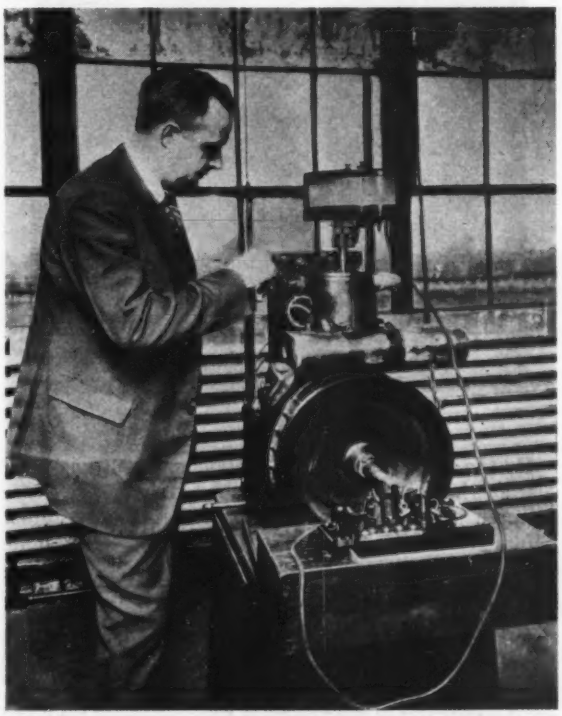
How their goal was achieved has been told many times before, and so here we will review their efforts only briefly. The long search was begun under Kettering's inspirational leadership in Dayton in 1916, soon after Midgley joined him after graduation from Cornell. The first milestone was the conclusion that the fuel, and not any mechanical defect in the engine, was responsible for knock.

The first antiknock agent to be discovered—purely by luck—was iodine. This prompted Midgley and his associates to believe that the color or some other physical property of gasoline might be to blame. Then came the basic discovery that the chemical properties of the fuel were involved, but this discovery raised more problems than it solved. At one time aniline seemed to offer a solution. Eventually the research team tried compounds of various elements, including metals, finally winding up with tetraethyl lead. The long search had taken Midgley and his colleagues up countless blind alleys that often brought their work close to abandonment. It cost General Motors more than $3,000,000.

Those who first worked with Midgley and Boyd on the project included Dr. Carroll A. Hochwalt, Dr. James P. Andrew, Charles P. Harding, and Russell D. Wells, and a few others concerned with related phases of the search. Most of them were to achieve further distinction in later life. Boyd became head of the Fuels and Lubricants Department of General Motors' Research Laboratories Division. Hochwalt is now vice-president in charge of research for the Monsanto Chemical Company. Before his death in 1944, Midgley was vice-president and general manager of Ethyl Corporation, largest tetraethyl lead manufacturer today. Kettering was to become, among his many other distinctions, the first president and a director of Ethyl.

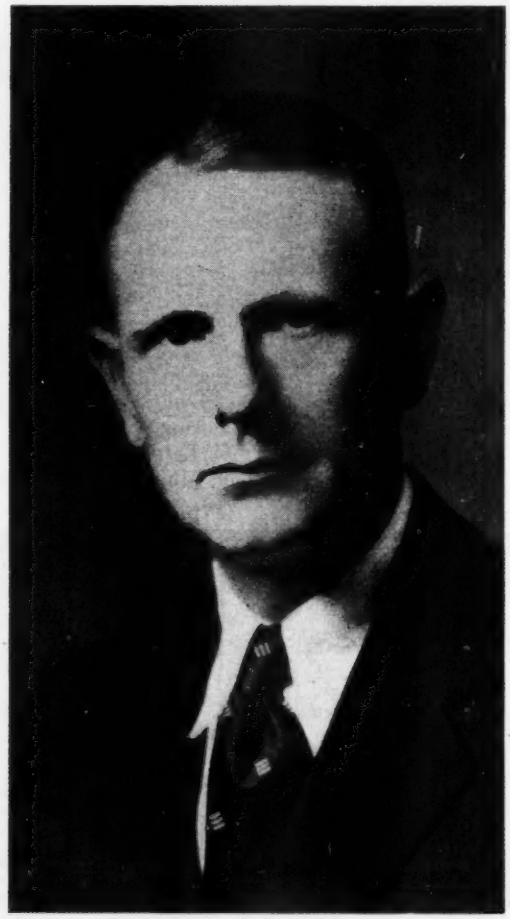
The cooperation of university personnel gave impetus to the search for an antiknock agent as early as 1917. The first assistance came from Ohio State University—from Dr. William E. McPherson and Dr. C. E. Boord, as well as from Dr. W. C. Ebaugh, head of the department of chemistry at Denison University. They made useful contributions to the exploratory work Midgley and his colleagues were doing with anilines and various other compounds containing nitrogen. Some of their work was carried out as part of a program which resulted in the successful development of a synthetic aviation fuel produced experimentally by Midgley and the others for the Government during World War I.

Somewhat later on, Henry C. Lord, professor of astronomy at Ohio State, assisted Midgley in building a



The Late Thomas Midgley, Jr., at the Laboratory Test Engine with Which the Antiknock Properties of Tetraethyl Lead Were First Established

spectroscope which was used to study combustion inside an engine during fuel knock. At another phase of the research, when it was believed that the problem should be approached with the understanding that the world's supply of oil would soon be exhausted, Dr. Harold Sibbert of Yale worked closely with Boyd and Hochwalt in exploring the possibilities of making a synthetic, knock-free fuel from cellulose.



T. A. Boyd

By the spring of 1921 the confidence of Midgley and his aides had reached its lowest ebb. In fact, the entire research project was scheduled for the scrap-heap just before Kettering's happy discovery of work being done by Professor Victor Lenher of the University of Wisconsin, who had been experimenting with selenium oxychloride as a "universal solvent."

Lenher's active cooperation helped Midgley and the others prepare and test the compound as an antiknock agent; at this point they were willing to try anything new. Although selenium oxychloride proved highly corrosive and therefore impractical, the discovery of its remarkable antiknock properties gave the discouraged men what they needed the most—fresh interest and enthusiasm.

Subsequent tests with an alkyl compound of the similar element, tellurium, offered still greater possibilities, but it presented a major antisocial drawback. Midgley, Boyd, Hochwalt, Andrews, and all the others radiated an overpowering garlic-like aroma from their contacts with the new experimental agent. In later years Midgley and his associates often commented laughingly on the fragrant aspects of this turn of their research—which, fortunately for the noses of the motorized transportation world, was finally dropped as impractical for a number of other reasons.

The spark which ultimately touched off the magazine of success earlier than it might have done came from the Massachusetts Institute of Technology through Dr. Robert E. Wilson, now chairman of the board of Standard Oil Company (Indiana). At that time, he was director of the Research Laboratory of Applied Chemistry at M. I. T. The laboratory was undertaking other research for General Motors, and Wilson had heard of Midgley's work. The two men were to become close friends as their paths joined. (They discovered in due course that they both were not only born in Beaver Falls, Pennsylvania, but had been delivered by the same physician.)

Dr. Wilson, describing how he approached Midgley with his novel idea, recalls that he "showed Tom a new chart of the periodic system I had drawn up, in which I had arranged the elements according to both their electropositive and electronegative properties in accordance with Langmuir's new octet theory, bringing out certain relationships which had not generally been appreciated.

"Tom was greatly interested in this, especially since he believed that the antiknock properties of various agents were primarily properties of the elements, and he had some indications that the antiknock effect of an element varied predictably with its location in the periodic system. The use of my chart of the elements was largely responsible for his trying tetraethyl lead."

Knowledge obtained in the search up to that time made it evident to Midgley that all elements yet found with knock-suppressing abilities were located at the far right of Dr. Wilson's electronegative arrangement of the table—in either the carbon, nitrogen, oxygen, or fluorine groups. It was also noted that the valence of the element in the compounds with antiknock properties corresponded with the number of vacant spaces in the outer shell of the element's electrons—iodine, one; selenium and tellurium, two; and nitrogen, three. From the knowledge that bromine increased knock while iodine reduced it, and that tellurium was much more powerful than selenium as a knock-suppressor, it was surmised that antiknock effect increased toward the bottom of each column.

Greatly excited by this new approach to their problem, Midgley and his associates, as they described it, "rolled up our sleeves for a systematic foxhunt." Ethyl, amyl, or phenyl compounds of the four groups of

elements were prepared for testing, and then classified in accordance with their knock-reduction abilities. As each exact rating was obtained, it was plotted on a three-dimensional graph called "The Peg-Board."

This graph consisted of a square board in which a peg was set at the point corresponding to the location of each element as arranged by Dr. Wilson, the height of each peg conforming with the degree of antiknock effectiveness of the element represented. On the graph it soon became apparent beyond question that effect upon knock was a periodic function of the elements. The high pegs showed clearly that the degree of effectiveness increased at the bottom of each group of elements. Compounds of Midgley's fragrant friend tellurium, for example, were the best in the oxygen group.

It was at last clear to the entire research group that they were on the right track. Interest soared to fever pitch as tests on the carbon group began. The first compound they tried was tetraethyl tin, on October 28 and 29, 1921. Results were so successful that a number of experiments were carried out during the following month. The compound, however, was found to induce preignition, and so they turned to lead, the lowest element in the group.

On the morning of December 9, Midgley, Boyd, Hochwalt, and the others proved that tetraethyl lead was the rainbow at the end of the trail. The ear-splitting knock of their test engine turned to a smooth purr when only a small amount of the compound was added to the fuel supply. All the men "danced a non-scientific jig around the laboratory." Midgley reported the discovery to Kettering at once. For hours the two men talked, planned, and dreamed.

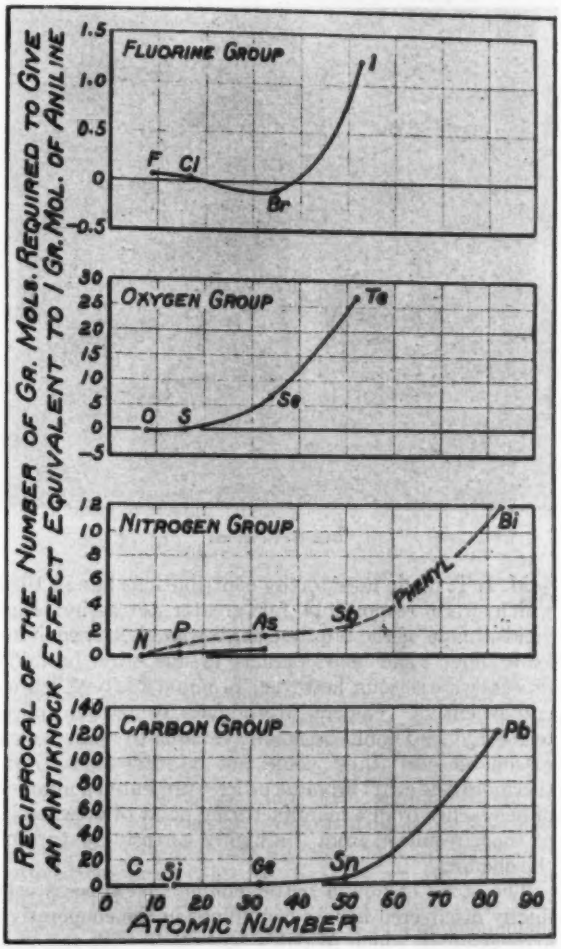
But as any chemist knows, long stretches of thorny terrain lie between a laboratory discovery and the production and marketing of a new chemical product. Tetraethyl lead was no exception. Kettering, Midgley, and others associated with the discovery and potential use of tetraethyl lead were deeply concerned over a satisfactory manufacturing process. It seemed to them that their infant progeny had a long road to travel before reaching mature commercial success.

The few cubic centimeters of tetraethyl lead Hochwalt had prepared for the initial tests had been made by synthesizing zinc ethyl and then dropping it on lead chloride. Later on the research group tried half a dozen other processes. None seemed to offer better commercial possibilities, and so for a time General Motors seriously considered building a 100-gallons-per-day tetraethyl lead plant which would use the zinc ethyl method. Dr. Wilson at M. I. T., however, was asked to explore the production problem further. Assisted by Dr. C. S. Venable and Dr. William G. Horsch, he investigated the possibility of making a suitable lead compound by the electrolysis of acetone in a sulfuric acid solution, using lead electrodes.

While the research at M. I. T. was still under way, Midgley reported his success in Dayton with a process involving the reaction of a sodium-lead alloy and ethyl iodide in the presence of a catalyst. On April 18, 1922, ethyl bromide was substituted for ethyl iodide, but with somewhat poorer yields of tetraethyl lead. Ethyl chloride was also tried but with no positive reaction whatever—the secret of this process was yet to be unlocked in the chemistry laboratory of Clark University in Worcester, Massachusetts.

Assurance that he was heading in the right direction was given to Midgley at this time by Dr. E. E. Reid, professor of chemistry at Johns Hopkins University. Dr. Reid was asked to make a critical examination of the chemical literature on the subject of organic compounds of lead, particularly on ways and means to obtain high tetraethyl lead yields. He reported that on the basis of his investigations, "the sodium-lead method or some modification of it is the most promising." The work on obtaining lead compounds by electrolysis at M. I. T. was therefore discontinued.

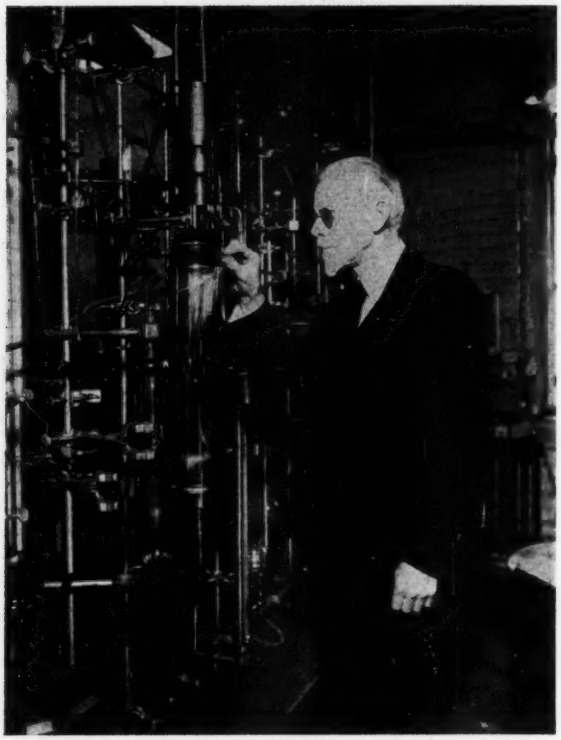
Refinements in the ethyl bromide process developed



Plot of the Antiknock Effects of the Elements in Four Groups of the Special Periodic System Used as a Guide in This Search

The vertical scales are different, but the rising antiknock effect toward the right in each group is apparent.

by the General Motors group in Dayton at length produced results almost as good as the ethyl iodide process —results made possible largely by the use of pyridine as a catalyst—but Midgley was not yet completely satisfied. Arrangments were made with M. I. T. to continue additional research on a still better way to make tetraethyl lead, so that General Motors could concentrate on adapting the new product to commercial use.



Charles A. Kraus

M. I. T. made noteworthy contributions late in 1922 which were responsible for greater tetraethyl lead yields. One of the improvements was a better sodium-lead alloy. The shortcomings of the ethyl bromide process were serious, however; bromine was both scarce and expensive. General Motors was aware that unless tetraethyl lead could be made available to refiners at a reasonable cost, they would not be interested. Furthermore, the ethyl bromide process presented a number of headaches from a manufacturing point of view, most of them resulting from the highly corrosive nature of the chemical.

The story of how a better commercial process was finally discovered has its beginnings in the cooperative arrangements which Midgley had made with research men at the Bayway, New Jersey, laboratories of Standard Oil of New Jersey some years before. This teamwork came about through Frank A. Howard, then active in the Society of Automotive Engineers and a consultant for Standard of Indiana and the Jersey company, who had read published accounts of the work Midgley and his associates were doing under Kettering's guidance. Howard discussed the antiknock research with Kettering and offered to try to interest both oil companies.

Eventually Howard left his Chicago practice to organize a Research, Development, and Patent Department for the Jersey company at Bayway. He had already persuaded the company to buy test engines and other equipment through Midgley. An aggressive attack on the problem of knock was started immediately, but, as Mr. Howard puts it, "Midgley and his crew were always one jump ahead of us."

Before a public announcement was made on General Motors' tetraethyl lead discovery, Midgley told Howard what the compound could do. Standard research men were asked to double-check and see if they had corresponding success. Every test that Standard made substantiated Midgley's findings and generated considerable enthusiasm throughout the Jersey company's research organization. Standard's research group, however, was quick to share with Midgley and his colleagues an awareness of the problems involved in the ethyl bromide process from a large-scale manufacturing standpoint.

Finally Dr. Edward B. Peck, a research chemist at Bayway, suggested that the laboratories consult Dr. Charles A. Kraus of Clark University. Peck had studied for his Ph.D. degree under Dr. Kraus at Clark, and was familiar with the nature and scope of his former professor's exhaustive investigations in the field of organo-metallic compounds. He was also aware of Dr. Kraus' more recent success in obtaining high yields of tetramethyl tin. It seemed to Peck and others at Standard that Dr. Kraus was without doubt better qualified than anyone else they knew to lend a helping hand.

A meeting of the American Chemical Society was held in New York a short time later. Here Peck discussed the problem with Dr. Kraus, who expressed a keen interest in seeing what he could do. A formal agreement was reached between Standard's laboratories and the Clark professor in the fall of 1922, when Dr. Kraus was employed as a research consultant. Inasmuch as Dr. Kraus planned to undertake his new investigations in his laboratory at Clark, he remained on the faculty and continued teaching his chemistry classes.

The first thing Dr. Kraus did was telegraph Dr. Conral C. Callis, a former graduate student, who had returned home after studying for his Ph.D. degree with Dr. Kraus at Clark. They had been making the investigations of methyl tin compounds together, and Dr. Kraus was confident that Callis could make valuable contributions to the new project.

Dr. Kraus' own interest in the physical and chemical properties of metals in solutions had gone back to his undergraduate days at the University of Kansas, where he had received his B.S. degree in 1898, and had continued during his years as graduate student, fellow,

research assistant, instructor, and professor at Kansas, Johns Hopkins, the University of California, and M.I.T. Some of his early investigations included the measurement of the conductance of metal solutions in liquid ammonia. In due course his research covered similar and related investigations involving the electrolysis of halides of organic derivatives of such metals as sodium, antimony, mercury, and tin.

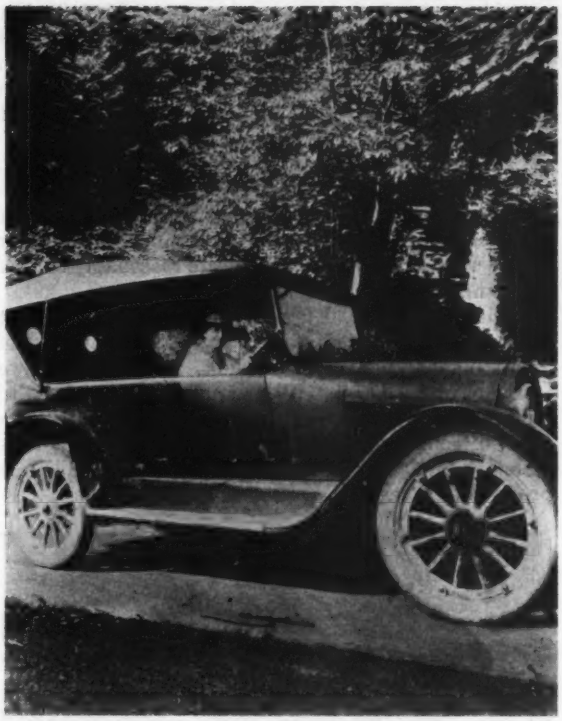
Speaking of how his research at Clark paved the way for his work in tetraethyl lead, Dr. Kraus states that

> ...after World War I, I decided to make a more thorough investigation of organo tin compounds, particularly methyl derivatives. I turned the job over to Callis, and he carried out the investigation for his Ph.D. degree.
>
> Our results with the new Grignard reaction were not very promising, and so we decided to begin by preparing trimethyl tin iodide by the reaction of sodium-tin alloy and methyl iodide, a process which I had used successfully many years earlier. This reaction proceeded satisfactorily after we learned that zinc acted as a catalyst when added to the alloy.
>
> We were confronted with a practical difficulty, because I had in mind carrying out rather extensive investigations with the methyl tin derivatives, and iodine at that time was a very expensive element. Even bromine was not too plentiful and was rather costly. Accordingly, I decided to carry out the reaction of the alloy with methyl chloride, which at that time was available on the market in cylinder form. We built an autoclave having a capacity of about three liters, charged it with alloy and methyl chloride, and allowed it to react.
>
> We found that we had to control the reaction by keeping it going for some time, about 24 hours, at 0° and then allowing the reaction to come up gradually to 100°. On allowing the reaction to stand for some time at any one temperature, the pressure fell as the methyl chloride was consumed, and so the temperature was raised to keep the pressure substantially constant. On heating to 100° for a period of time, virtually all the methyl chloride was used up and practically quantitative yields of tetramethyl tin were obtained.

This was the point which the investigations of Dr. Kraus and Dr. Callis had reached at the time they began their work on tetraethyl lead. It was here that Dr. Kraus' rich academic background of some 25 years of pioneering was to become invaluable.

Dr. Kraus is exceedingly modest in describing his deductive reasoning as applied to the challenge of tetraethyl lead. The incisiveness of his approach can be appreciated only in the light of how little was then generally known about organo-metallic compounds. With little reference material to depend upon aside from their own experience, Drs. Kraus and Callis were able to apply at once the purest of academic research to the successful solution of an undertaking far more significant than they realized at the time. Dr. Kraus recalls:

> When Callis came back to the laboratory at Clark in the fall of 1922, we decided to proceed on the basis of our experience with tin compounds. It seemed logical to us that if alkyl halides like methyl iodide and methyl chloride in reaction with sodium-tin alloy would produce satisfactory yields of tin halides, we would do well to attempt to make tetraethyl lead with some suitable member of the alkyl halide family.
>
> Inasmuch as bromine and iodine were both expensive, and my job was to find a process which would be commercially practical, it seemed to us that the reaction of sodium-lead alloy and ethyl chloride represented the only practical solution.
>
> Neither one of us was familiar with tetraethyl lead. We made



Automobile in Which the First Road Tests on Antiknock Fuel Additives Were Made, 1921

The compression ratio of the engine of this Chevrolet was stepped up to 7:1 from the normal ratio of 4.1:1. Fuel used contained 9 per cent of ortho-toluidine by volume. The car was called "The Goat," because of its hill-climbing ability and because of the musty smell of its exhaust, containing what was then the best antiknock agent to be discovered.

it in experimental quantities by the established method of reacting sodium-lead alloy and ethyl iodide while we were getting together the necessary apparatus and materials. I might say that we had little to go on. We designed and built all our equipment ourselves. The first thing we made was an autoclave of about three-liter capacity from a section of heavy steel tubing, about 15 inches long and about four inches in diameter, as I remember it. I did the welding myself.

We attached a motor with a chain drive to the autoclave in order to revolve it while the reaction was taking place. Inside the autoclave we had steel balls about the size of large marbles so that the mixture could be agitated. The reaction was allowed to proceed to completion under pressure, which required about six hours. Tetraethyl lead was then separated from this reaction by steam distillation.

Dr. Kraus actually made two significant contributions to commercial production of tetraethyl lead during the course of his investigations. He not only proved the practicality of the low-cost ethyl chloride process, but in showing that the composition of the alloy was a critical factor, he developed a more economical sodium-lead alloy containing a small proportion of sodium. With ethyl chloride he found the best alloy had a composition corresponding to the formula $NaPb$, and that it was unnecessary to add a catalytic agent.

It will be recalled that Midgley had also tried ethyl

chloride, and so had the research group at M. I. T., but they had used sodium-lead alloy in the proportions of Na_4Pb and Na_2Pb_4. These alloys were reactive with ethyl bromide in the presence of a catalyst, but with ethyl chloride the results were so disappointing that this approach had not been explored any further.

"Very encouraging results" were obtained by Drs. Kraus and Callis from their first experiments. Before long their tetraethyl lead yields averaged from 70 per cent to 75 per cent, and occasionally hit as much as 85 per cent. Within six months they were reasonably sure of the commercial applications of their process.

"Thereafter," Dr. Kraus concludes, "a small pilot plant was constructed at Bayway with a capacity of about one-half gallon of product, and with this we worked out further details for applying the process to larger-scale operations. Our work was only preliminary, of course, and it remained with subsequent commercial manufacturers to adopt our process to full-scale production."

Early Apparatus for Manufacture of Tetraethyl Lead

For this process the entire motorized transportation industry owes an enormous debt of gratitude. The Kraus-Callis process has been refined and improved in a number of ways during subsequent years, but it is still the basis for all tetraethyl lead manufacturing today. It is one of the few industrial chemical processes so fundamentally sound that it has not required drastic revision since it was first introduced.

The next step on the road to commercial applications was undertaken by Standard Oil of New Jersey. It built a larger pilot plant at Bayway, using the Kraus-Callis process, and introduced a number of engineering refinements. Then the General Motors Chemical Company was organized in 1923 to market the new product, which had been introduced successfully with the first public sale of "Ethyl" gasoline in Dayton on February 2 of that year.

By 1924 the time seemed ripe for the consolidation of all results of antiknock compound research, in order that a more concentrated effort could be made to develop the general use of the new product. General Motors, with its discovery of the use of tetraethyl lead, and Standard Oil of New Jersey, with its efficient Kraus-Callis process, decided to pool their mutual interests and set up a jointly-owned company to take charge of the whole enterprise. This company was incorporated in Delaware in August of 1924, and is now Ethyl Corporation.

A number of problems still remained for the new company, in spite of all the obstacles already overcome. One of the most formidable difficulties was finding enough bromine to manufacture the ethylene dibromide required in "Ethyl" antiknock fluid, the trade name Kettering recommended for the finished product. Bromine and chlorine compounds were found to be highly useful as halogens in removing potential lead deposits from engines burning gasoline containing the antiknock agent, but only limited quantities of bromine were available at high cost in the United States. A concession to extract the element from the waters of the Dead Sea was considered seriously at one point.

Finally a conviction that it would be practical to remove bromine from ordinary sea water developed from experimental work at Ethyl and at General Motors. This highly unique idea—the first attempt to obtain valuable substances from the ocean's limitless store—was then tried with some success at a semi-works plant built for Ethyl at Ocean City, Maryland.

The practicality of the process was definitely established in April of 1925 in a "floating laboratory" on board a converted Great Lakes freighter rechristened as the good ship "Ethyl." It sailed from Wilmington, Delaware, some 250 miles out into the Gulf Stream, but it was anything but a pleasure cruise. Seasickness knocked out most of the landlubber crew of chemical workers, which meant they were able to operate the experimental equipment for only a limited time. Even so, the venture proved successful enough in terms of concrete results. About 100 pounds of bromine were obtained, and no one regretted the half-million dollar cost involved.

Subsequent cooperation by the Dow Chemical Company brought about still more advantageous bromine extraction methods, eventually leading to the formation of the Ethyl-Dow Chemical Company. Ethyl-Dow built the first full-scale bromine extraction plant at Kure Beach, North Carolina, and later a more modern plant at Freeport, Texas, using sea water from

the Gulf of Mexico. The Freeport plant is now the largest producer of bromine in the world.

The original process, briefly, began with treating incoming sea water with sulfuric acid and chlorine gas, so that bromine was set free in a dilute solution. The bromine was next blown out of solution by countercurrents of air in towers, and then absorbed from the air in adjoining towers by passage through a spray of soda ash solution. After the soda ash solution was recirculated until it contained a high concentration of bromine, the solution was treated with sulfuric acid and steam, giving up its bromine in liquid form. Ethylene dibromide was then manufactured by reaction of the bromine with ethylene. Certain improvements have been made in this process in recent years.

It is well worth pointing out here that Ethyl Corporation's pioneering efforts in "mining" the ocean helped pave the way for the remarkable success of Dow in removing magnesium from sea water, a large and highly important process today. The Dow magnesium plant at Freeport, as well as the Ethyl-Dow bromine plant nearby, have attracted considerable interest among industrial chemical engineers and among college and university chemists concerned with applying laboratory processes to commercial use.

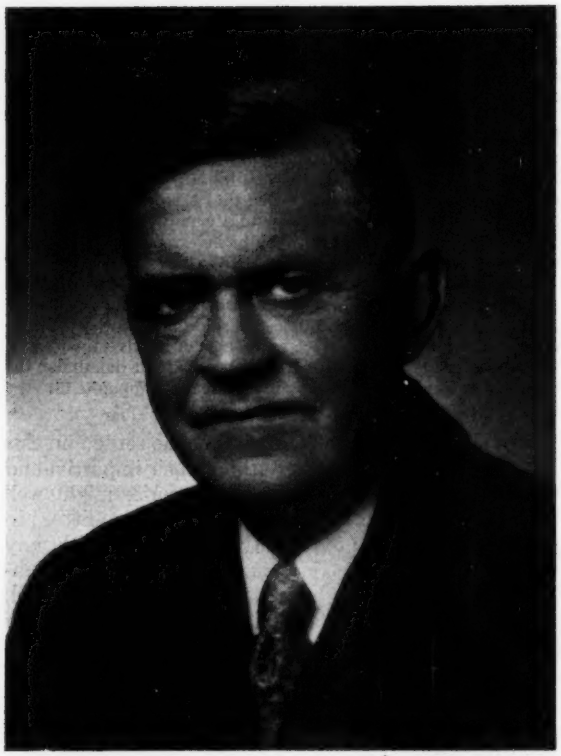
The bromine problem had no sooner been cleared away, however, when startling developments threatened to wreck the new industry completely. Newspaper publicity in May of 1925 focused public attention on several deaths caused by lead poisoning among those exposed to tetraethyl lead during its manufacture and handling.

An analysis of these developments, together with comments on work done at the University of Cincinnati leading to the elimination of such hazards, has been prepared by Dr. Robert A. Kehoe for inclusion in this article. Dr. Kehoe is director of the Kettering Laboratory of Applied Physiology in the Department of Preventative Medicine and Industrial Health at the university's Medical School, and has been director of the Medical Department of Ethyl Corporation since the department was organized in 1925. Dr. Kehoe states:

> There had been prior evidence of hazards involving tetraethyl lead, and a careful study of the problem had been undertaken, but the problems of human exposure and their means of control had not yet been fully appreciated. It is to be remembered in this connection that the production of tetraethyl lead on a laboratory scale for experimental purposes had provided no more than the mildest warning of the toxic characteristics of the product, and the risk of going over to a larger scale production had not been fully evaluated.
>
> Moreover, the several circumstances, which, in retrospect, should have given the warning, were represented by a series of incidents which occurred at widely separated points within a comparatively short period of time, and so were not put together to form the evidence which was soon to be available. With better appreciation of these hazards, control measures could be and were applied, but unfortunately the rude shock of tragedy was required to focus the attention of the several groups involved upon the true nature of the occupational hazard.
>
> From the aspect of this account, the major significance of the events of May, 1925, lay in the fact that they created in the public mind an apprehension concerning hazards associated with the distribution and use of leaded gasoline, which, while wholly unjustified, was so great and so widespread as to require official action on the part of the health authorities of the United States Government.
>
> The potential public health hazards in the use of leaded gasoline had been taken into consideration by the General Motors Chemical Company as early as 1923, when investigations by the United States Bureau of Mines were initiated and sponsored by the Company, but it was recognized that these, as differentiated from manufacturing hazards, were of a wholly different order of magnitude, and, while well worthy of investigation, were hypothetical in character.
>
> Nevertheless, on the heels of the tragedy in May of 1925, Ethyl Corporation voluntarily withdrew its product from the market, and no "Ethyl" gasoline was sold on its authority until June of 1926, after the issuance of a report of an investigation by the United States Public Health Service, carried out under the direction of a committee of prominent scientists appointed by the Surgeon General of the Public Health Service.

The industry owes much to those who served on this investigating committee. Without their impartial and unbiased conclusions, the whole enterprise might well have been crippled. Members of the committee, in addition to those not directly associated with any specific university or college, included such distinguished faculty members as William H. Howell, professor of physiology at the Johns Hopkins School of Hygiene and Public Health, chairman; David L. Edsall, Dean of Harvard Medical School; Reid Hunt, professor of pharmacology at Harvard Medical; W. S. Leathers, professor of preventative medicine at Vanderbilt University; Julius Stieglitz, professor of chemistry at the University of Chicago; and C. E. A. Winslow, professor of public health at Yale.

> The essential conclusion of the committee [Dr. Kehoe continues] was to the effect that "there are no good grounds for prohibiting the use of 'Ethyl' gasoline of the composition specified as motor fuel, provided that its distribution and use are controlled by proper regulation." This authoritative opinion paved the way not only for the resumption of the antiknock compound business, but also for the self-regulation of the industry, which, since its resumption, has guarded jealously the safety of its employees and ... of its customers.
>
> The regulations believed by the committee to be necessary were proposed mainly in the form of principles, and these were put into effect in fact and in spirit by the new industry. They were further developed in detail and application on the basis of a unique activity initiated in the physiology department of the College of Medicine of the University of Cincinnati in 1925. The Ethyl Corporation financed an extensive experimental program in the University of Cincinnati, which because of its conduct in an institution responsible to the public, gained public and official acceptance in the United States and abroad.
>
> On the basis of continuing investigations, the occupational hazards of the tetraethyl lead industry and the potential hazards of the public were subjected to critical examination and rigid control. The work so initiated led to the development of what is now the Kettering Laboratory in the Department of Preventative Medicine and Industrial Health of the University of Cincinnati, in which many problems of industrial health have been and are being investigated under the sponsorship of many industrial organizations.
>
> Work of this type is being continued there by Ethyl Corporation in order to keep well in advance of any hygienic threat to its business and to its customers. Meanwhile, Ethyl takes a justifiable pride in the important part it has had in the development of this center for medical research and instruction in the field of industrial health.



Pach Bros., New York

Graham Edgar

Thanks to the work of the Kettering Laboratory, the information required to control the hazards of the manufacture and transportation of Ethyl's products and to protect those associated with the preparation, distribution, and use of leaded gasoline has been provided and put to work, with highly satisfactory results to Ethyl, its customers, and the consumers of its products.

The tremendous importance of the contributions made by the University of Cincinnati and by Dr. Kehoe and his staff, both at the Kettering Laboratory and within Ethyl Corporation itself, can be appreciated only when it is borne in mind that the antiknock-compound industry might not even exist today without the work they have done and are still doing. The university can therefore be credited with the salvation of a new and invaluable enterprise on the American industrial scene, and with insuring a work environment for an industry which has done so much to make better motorized transportation possible.

In its first year Ethyl Corporation was well aware of the fact that a continuing research and development program would always be a highly essential part of its relationships with the oil and automotive industries. Not only were there current problems still unsolved, but the firm anticipated the inevitable challenges of a future in which Ethyl intended to pioneer and maintain its leadership. The company therefore asked Dr. Graham Edgar, former professor of chemistry at the University of Virginia, to head its research activities.

Dr. Edgar had been in charge of research for Ethyl's immediate predecessor, the General Motors Chemical Company. He brought with him a rich background of academic understanding and long experience in chemical research. This was soon put to use in his work on obtaining bromine from sea water, and then on his supervision of a basic research project directed toward an understanding of the mechanism of combustion of pure hydrocarbons. The results obtained served as an inspiration for much of the subsequent work in this field. Such studies are now in progress in many laboratories.

Another outstanding contribution by Dr. Edgar was synthesis of the nine isomeric heptanes in order that their molecular structure might be correlated with antiknock quality. Among these was 2,2,3-trimethylbutane, later named triptane. It was found that after the addition of tetraethyl lead, triptane had higher antiknock quality under some conditions of engine operation than any other compound that had been evaluated.

The former University of Virginia professor is perhaps best known in petroleum circles as the man who invented the familiar octane scale for expressing the antiknock quality of gasoline. He developed this now commonly accepted yardstick shortly after he joined Ethyl Corporation, and today the term "octane number" as a measure of gasoline power potential is at least generally understood by virtually everyone who drives a car. Dr. Edgar retired as a vice-president of Ethyl in 1952.

Despite all the work done by Midgley, Boyd, and their associates, the new company faced formidable problems during its early years with the utilization of tetraethyl lead. Boyd at General Motors had already found out that chlorine and bromine compounds were helpful, and M. I. T. had worked closely with Midgley on utilization problems. Early in 1924 Dr. Wilder D. Bancroft of Cornell had been retained by General Motors as a consultant for any aid he might give, but although their collective efforts had certainly brought progress, considerable work remained to be done.

The difficulty with tetraethyl lead was that the useful life of exhaust valves and spark plugs was drastically shortened when engines used gasoline containing the antiknock agent. In general, automotive engineers did not yet visualize the potential benefits of the new product in properly designed engines, but they were quite sensitive about its undesirable effects in existing engines. Ethyl Corporation therefore found itself between Scylla and Charybdis—able to solve the problem of fuel knock on the one hand, but accused on the other of creating conditions which neutralized the advantages of the fuel additive. Tetraethyl lead threatened to become "the product that nobody wanted."

Late in 1923 and early in 1924 work on overcoming exhaust valve difficulties and certain related problems was undertaken at M. I. T., under the supervision of W. G. Whitman and Robert T. Haslam, assisted by others. Mr. Haslam is now a director of Ethyl Corporation, an industrial chemical consultant in New

York, and a life member of the M. I. T. Corporation.

The officers of the Ethyl Corporation became convinced that tetraethyl lead would never be accepted merely by waiting for the automotive industry to become aware of its value and for automotive engineers to solve the problems created by its use. Accordingly they turned once more to a university for help.

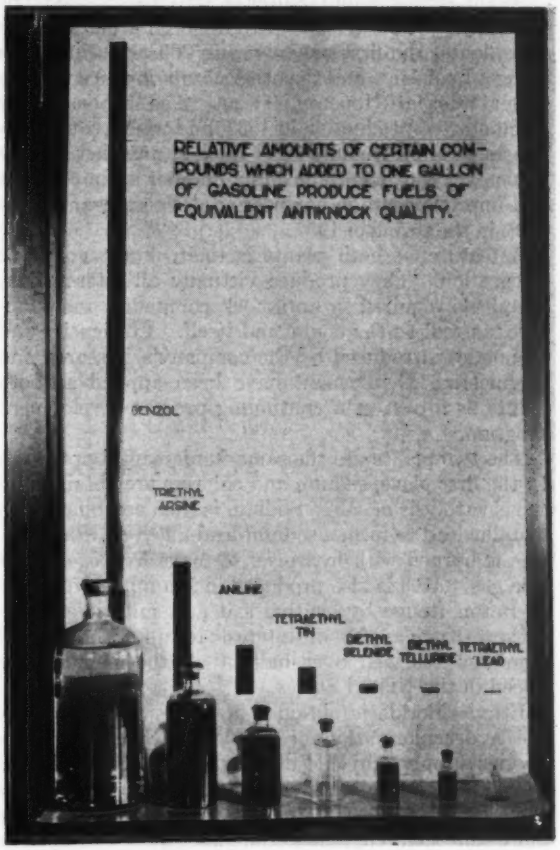
As an instructor in mechanical engineering at Harvard, Earl Bartholomew had investigated for an automobile company certain coatings for the combustion chambers of engines. The inventor of these coatings claimed they were effective in catalyzing combustion and reducing knock. Bartholomew had thus developed an interest in controlling combustion by chemical means, and joined the research staff of Ethyl Corporation in 1926.

A broad assignment was given him, including evaluation of the potentialities of higher compression ratios in automotive engines, and solution of the problem of the short life of engine parts affected adversely by antiknock fluid in gasoline. A year later he became director of automotive engineering research for Ethyl and established a new laboratory in Detroit, in the center of the automobile industry. A comprehensive experimental program was then started, destined to have far-reaching effects on the formulation of antiknock fluids, the design of automotive engines, and the choice of materials for engine construction.

Bartholomew and his associates found that the unwanted effects in engines were results of a number of different chemical reactions involving the products of antiknock fluid combustion and engine components. They also found that the occurrence and severity of these reactions were closely related to the quantities and proportions of ethylene dibromide and ethylene dichloride that might be used in combination with tetraethyl lead. In 1928 a drastic change was made in the composition of the antiknock fluid, reflecting the knowledge obtained in this research and greatly increasing the compatibility of antiknock fluid with engines.

But modification of the antiknock material alone was not sufficient to bring about satisfactory operation essential to the product's enthusiastic acceptance by the automotive industry. It was apparent that an equal if not greater opportunity existed for joint effort by Ethyl Corporation and the automotive industry in adapting engines to the antiknock compound. Accordingly the company's laboratories at Detroit, and later at San Bernardino, California, delved deeply into metallurgy, ceramics, and the configuration of engine components. Coordination of these two lines of attack —on the antiknock product and on engines—was successful, until tetraethyl lead finally became generally recognized as essential to automotive progress.

With the passing of the years, the company's research in these fields has expanded, and has become still more closely integrated with the technical programs of the oil and automotive industries. The problems of fuels, oils, and engines have become so enmeshed that they are inseparable. These problems are never solved permanently, inasmuch as each advance in power production tends to reactivate old problems and to create new ones. Since 1928 Ethyl Corporation has made a series of changes in the composition of its antiknock fluids in recognition of modifications of the environment in which fuels are burned in engines. These changes have had the further advantage of enabling the sale of antiknock compounds at substantially lower prices.



The Minute Amount of Tetraethyl Lead Needed for a Given Antiknock Effect by Comparison with Some Other Compounds

The tetraethyl lead industry settled down to more orderly expansion by the close of the 1920's. Although it has conducted most of its own research since that time, Ethyl Corporation, for example, has continued to look to college and university laboratories for supplementary aid along some lines. Ethyl has turned to Purdue University, the University of Illinois, and the University of Michigan for fundamental work on the Kraus-Callis process. M. I. T. is undertaking certain phases of combustion research which it can conduct advantageously. Studies on the utilization of sodium, other than in the sodium-lead alloy for tetraethyl lead manufacture, have been made for Ethyl at a number of educational and commercial research centers.

The manufacturing, distribution, storage, and blending facilities associated with the antiknock compound industry today have their origins, of course, in the historical panorama we have sketched here. That these facilities must be extensive can be realized by the mere statement that tetraethyl lead is used in more than 95 per cent of all gasoline on the market, and that the national consumption of motor and aviation gasoline is now about 48 billion gallons per year.

As the largest manufacturer of antiknock compounds containing tetraethyl lead, Ethyl Corporation operates two plants, the first one covering 200 acres in Baton Rouge, Louisiana, and the other occupying 80 acres of a larger tract at Houston, Texas. The Baton Rouge Plant started production in 1937, and with frequent expansion, is now the largest of its kind anywhere. The Houston Plant, incorporating a number of innovations and improvements in engineering design, began operations in the spring of 1952.

A feature of both plants is their almost complete integration. They produce virtually all intermediate chemicals required in antiknock compound manufacture, as well as the compound itself. Efficiencies and economies introduced by the company's Research and Engineering Department have been applied at both plants as a part of a continuing process development program.

The two plants use the same fundamental processes. In the first place, sodium and chlorine are obtained by the electrolysis of salt. Sodium is then combined with metallic lead to form a sodium-lead alloy, and the chlorine is burned with hydrogen to make hydrogen chloride gas. HCl is also produced in Mannheim furnaces at Baton Rouge by heating salt and sulfuric acid together. It may be of interest to note that Ethyl manufactures well over half of all the sodium produced in the United States.

Ethyl chloride is obtained in refinery-type units by the hydrochlorination of ethylene. Neighboring refineries supply ethylene directly, but in Baton Rouge the plant can also crack refinery gas for a supplementary ethylene feed. In Houston the ethylene stream is more concentrated, and so the plant there can operate at lower pressures. With its two plants, Ethyl is now the world's largest ethyl chloride manufacturer. Ethylene dichloride is made at both plants by chlorinating ethylene.

Tetraethyl lead manufacture under the Kraus-Callis process begins in autoclaves charged with particles of sodium-lead alloy and with ethyl chloride. After the required reaction time—considerably shortened in recent years—raw tetraethyl lead is removed from the reaction mass by steam distillation. The product is then purified by aeration before it is piped to the blender. Unreacted lead is recovered from sludge and used again in subsequent alloy production.

In the blending operations, exact proportions of ethylene dichloride, ethylene dibromide, identifying dyes, and small amounts of other ingredients are added to form the finished antiknock compound, which includes about two-thirds tetraethyl lead by volume. The product is then shipped by tank car or drums to refineries for addition to gasoline via blending equipment ordinarily designed by Ethyl engineers.

The other manufacturer of antiknock compounds in the United States is E. I. du Pont de Nemours & Company, which operates a plant at Deepwater Point, New Jersey, as part of its Chambers Works. Before 1948 du Pont was licensed by Ethyl Corporation to operate under Midgley's patents and the Kraus-Callis patents which Ethyl had acquired from General Motors and from Standard Oil of New Jersey.

The tetraethyl lead and antiknock compound industry, as might be expected, has introduced a number of efficiencies, economies, and improvements in its basic manufacturing steps down through the years. The Ethyl Corporation's process for making ethyl chloride, for example, was pioneered at its Baton Rouge plant, and is accepted as the most modern way to manufacture this versatile product. Coincidentally enough, among those from the Standard Oil Development Company who contributed to the work on the process was Cecil L. Brown, one of Dr. Kraus' former graduate students.

All those from the many colleges and universities who have done so much in so many ways to make this completely American industry a reality are entitled to share full satisfaction in the realization that no more economically practical way has yet been found to improve gasoline quality than the addition of less than $^1/_{10}$ of one per cent of tetraethyl lead.

Neither should we pass over lightly some of the more indirect contributions which can be credited at least in part to the efforts of university research men who worked on the antiknock problem. The important discovery that branched-chain hydrocarbons are much better engine fuels than straight-chain hydrocarbons was made in Ethyl's laboratories during the course of the long investigations on the cause and cure of fuel knock. This basic information, first revealed by the discovery of the antiknock properties of isooctane by the University of Virginia's Dr. Edgar, lies behind modern methods of refining, and has helped make better gasolines possible.

In the sense that the tetraethyl lead industry has helped create other important industries like those which extract bromine and magnesium from the ocean, men from academic circles who helped establish the gasoline additive business can also share the credit for widening these horizons of industrial chemistry. Tetraethyl lead manufacturers in turn have themselves made a number of fundamental contributions, of course, to the technique of putting chemistry to work for mankind. Recent products developed at Ethyl, for example, are an ignition control compound for stepping up the operating efficiency of gasoline engines, and an ignition improver for diesel engines.

Dr. Kraus is among those in academic circles who

have followed the growth and development of the antiknock compound business with particular interest. Today he is professor of chemistry emeritus and former director of chemical research at Brown University, where he joined the faculty in 1924 after leaving Clark. He continues as a consultant for Ethyl Corporation and Standard Oil of New Jersey.

During World War II he served as consultant for the Manhattan District's atomic bomb project, operating a laboratory at Brown, where most of his work was concerned with chemical phases of the magnetic separation process.

He also contributed to the development of the oxygen rebreather in conjunction with the Naval Research Laboratory; the rebreather was used on aircraft carriers. For this Dr. Kraus received the Navy's Distinguished Public Service Award, the highest honor the Navy confers on a civilian.

Retirement, by the way, is only a word in Dr. Kraus' dictionary—every day he is at work in his laboratory, continuing his researches in the field of electrolytes and other problems.

It is interesting to note that fate gave Midgley and Kraus considerably more in common than their fundamental discoveries relating to tetraethyl lead. Midgley's death after an attack of polio cut short his career a decade ago, but they both served as president of the American Chemical Society and were destined to receive the society's most distinguished award—the Priestley Medal—as well as the Nichols Medal and the Willard Gibbs Medal from the A. C. S.'s New York and Chicago Sections. Each man has also been honored by medals from the Franklin Institute and with degrees by leading colleges and universities.

What is perhaps still more interesting, in the light of the recognition they have won in the field of chemistry, Midgley was trained as a mechanical engineer and Kraus as an electrical engineer. As the retired Brown University professor puts it, with a quizzical smile—"Is there such a thing as knowing *too much* chemistry?"

ADDITION OF SOLIDS TO A SEALED SYSTEM

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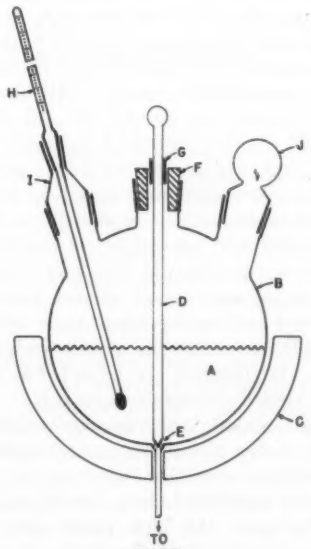
In many instances, it is desirable to add a solid substance to an evacuated or otherwise enclosed system. The accompanying diagram pictures a convenient apparatus for such manipulation whereby the solid (*A*) is first melted in a standard-taper (24/40) flask (*B*) of convenient size by means of a Glas-col heating mantle (*C*). Addition of the molten material to the desired system is controlled by adjusting the glass rod (*D*), the point of which has been ground with powdered carborundum into the opening of the outlet tube (*E*) protruding through the bottom of the mantle. The upper portion of the rod is sealed by means of a 24/40 to 10/40 standard-taper reducing adapter (*F*) into which has been inserted a short length of well lubricated Tygon tubing (*G*) of appropriate diameter. A thermometer (*H*) with an appropriate adapter (*I*) allows measurement of the temperature of the melt, which is kept constant by means of a Variac attached to the mantle. A 24/40 standard-taper glass stopper (*J*) occupies the third neck of the flask and provides for subsequent refilling of the apparatus.

The above apparatus proved especially useful for the continuous addition of solid substances to an evacuated dehydrogenation column.



[1] Present address: Blockson Chemical Company, Joliet, Illinois.

A NEW QUALITATIVE IDENTIFICATION PROCEDURE FOR COBALTOUS AND NICKELOUS IONS

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In most modifications of the Fresenius (hydrogen sulfide) scheme of qualitative analysis, cobaltous ion is identified in the presence of nickelous ion. While nickelous ion is easily identified by the dimethylglyoxime test, the tests for cobaltous ion are generally not so unambiguous. The procedure and identification test described here reveals cobaltous ion alone or in the presence of much nickelous ion by selective color formation. Cobaltous ion was found to form a deep blue solution with an excess of monothiophosphate ion, PO_3S^{-3}, in a solution to which sodium acetate has been added to make it slightly alkaline. Under these same conditions nickelous ion forms a greenish-white precipitate, which does not interfere with the formation of the cobaltous-monothiophosphate compound. Where nickelous ion concentration is sufficiently high to impart a greenish hue to the test solution, the blue cobaltous solution is readily observed after filtering. As the cobaltous-monothiophosphate compound proved to be completely soluble under these conditions only when the ratio of monothiophosphate ion to cobaltous ion is approximately 3:2 or greater, complex ion formation is indicated rather than simple salt formation.

PROCEDURE

The ions of the alkaline sulfide precipitation group—nickelous, cobaltous, ferric iron, ferrous iron, manganous, aluminum, chromic, and zinc—are precipitated in the usual manner by passing gaseous hydrogen sulfide into an ammoniacal solution of the filtrate from the acid sulfide precipitation group. All the sulfides or hydroxides obtained are soluble in cool 1:9 (approximately 1.2 *M*) hydrochloric acid, except the sulfides of nickel and cobalt, which are very slowly soluble and are filtered off to be subsequently dissolved in aqua regia. The ions put into solution by the dilute hydrochloric acid are isolated and identified by conventional procedures. After evaporating the aqua regia solution containing nickel and cobalt almost to dryness, and diluting to 10–15 ml., one gram or more of solid sodium acetate is added to make the solution slightly alkaline to litmus. The solution is boiled for one minute, filtered, and cooled to room temperature. To one-half of the filtrate is added, with vigorous shaking, 0.1 to 0.2 gram of anhydrous trisodium monothiophosphate. A deep blue solution identifies cobaltous ion, although in the presence of much nickelous ion the solution should be filtered to make the blue color more discernible. Dimethylglyoxime in alcohol solution is added to the other portion, and nickelous ion is identified by the well known bright red precipitate. In the presence of much cobaltous ion, the red precipitate is more easily seen by filtering off the brownish solution formed by dimethylglyoxime with cobaltous ion.

PREPARATION OF THE REAGENT

Anhydrous trisodium monothiophosphate, Na_3PO_3S, is much more stable than the hydrated salt reported in the literature.[1] It is readily prepared in a pure state by heating a concentrated aqueous solution of sodium hydroxide with thiophosphoryl chloride, $PSCl_3$, in the mole ratio of 6:1, respectively. The reaction of 40 grams of sodium hydroxide in solution and 17.5 ml. of thiophosphoryl chloride is carried out under reflux at 110–115°C. for fifteen minutes or more until the thiophosphoryl chloride layer has disappeared. The reaction products, trisodium monothiophosphate and sodium chloride, separate out on cooling in an ice-water bath. The solid salts are filtered off and dissolved in a minimum quantity of warm water, and the trisodium monothiophosphate is precipitated out by adding about 185 ml. of anhydrous methanol for each 100 ml. of aqueous salt solution. This precipitation is repeated and the solid salt dehydrated by suspending, with constant stirring for one hour, in 200 ml. of anhydrous methanol. The anhydrous trisodium monothiophosphate is filtered dry with suction, and is stable and nondeliquescent at ordinary relative humidities.

Thiophosphoryl chloride is conveniently prepared[2] by reaction of 54.6 ml. of phosphorus trichloride with 20.1 grams of powdered sulfur under reflux, with approximately two grams of anhydrous aluminum chloride added as catalyst. The reaction is often very vigorous after it is initiated with slight heating, so the reacting proportions must be kept small. When the reaction has subsided, the mixture of products is distilled, and the fraction at 120–125°C. collected.

DISCUSSION

The reaction of monothiophosphate ion with mixtures of cobaltous and nickelous ions in various mole ratios was investigated over wide concentration ranges, with the results shown in the table. Where nickelous ion concentration is high, a precipitate forms after several minutes. In all solutions containing cobaltous or nickelous ions a dark precipitate forms after several

[1] Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1947, Vol. VIII, pp. 1068–9.

[2] Knotz, F., *Österr. Chem. Ztg.*, 50, 128 (1949).

Reaction of Monothiophosphate Ion with Mixtures of Cobaltous and Nickelous Ions[a]

Mole ratio		*Total moles, $Co^{++} + Ni^{++}$*			
Co^{++}	Ni^{++}	*0.055*	*0.0055*	*0.00055*	*0.000055*
0.00	1.00	Gr.-wht. ppt.	Gr.-wht. ppt.	Gr.-wht. ppt.	Gr.-wht. ppt.
0.09	0.91	Gr.-bl. ppt.	Bl.-gry. ppt.	Purple soln.	Fnt. pur. soln.
0.18	0.82	Bl.-gr. soln.	Blue soln.	Blue soln.	" " "
0.27	0.73	Blue soln.	" "	" "	" " "
0.36	0.64	" "	" "	" "	Fnt. blue soln.
0.46	0.54	" "	" "	" "	" " "
0.54	0.46	" "	" "	" "	" " "
0.64	0.36	" "	" "	" "	" " "
0.73	0.27	" "	" "	" "	" " "
0.82	0.18	" "	" "	" "	" " "
0.91	0.09	" "	" "	" "	" " "
1.00	1.00	" "	" "	" "	" " "

[a] Results obtained when 0.1–0.2 gram of anhydrous trisodium monothiophosphate is added to approximately 10 ml. of the following cobaltous ion-nickelous ion solutions previously made alkaline with 1 gram of sodium acetate, boiled, and cooled.

hours, presumably cobaltous or nickelous sulfides. The dark precipitate is obtained quickly if the solution is heated. Without the treatment with sodium acetate and boiling, iron was found to interfere by the formation of a dark precipitate that obscured the blue color of the cobaltous test. The iron had evidently remained in trace amounts in the cobaltous and nickelous sulfides after treatment with the dilute hydrochloric acid. Ferric iron, the only form of iron present after the aqua regia treatment, is completely removed along with aluminum ion as the insoluble basic acetate by the hydrolysis. None of the other ions in the group are completely precipitated by this treatment.

Each remaining cation in the alkaline sulfide group was tested with monothiophosphate ion for color formation with the following results: ferric iron, dark brown precipitate; manganous, white precipitate; aluminum, white precipitate; and zinc, white precipitate. Chromic ion does not form a precipitate, and is changed very little in color by the monothiophosphate ion. The color of the solution is that of chromic ion alone—dull bluish-green by daylight, and dull reddish by incandescent light. It should have been removed completely by the usual separation methods prior to the nickel and cobalt identification tests, but its color would not be mistaken for that of the cobaltous-monothiophosphate compound, especially under incandescent lighting.

Mixtures containing all the ions, and unknown mixtures containing various ions of this group were satisfactorily analyzed by this method, with cobaltous and nickelous ions easily identified in each case.

ACKNOWLEDGMENT

The research of which this study is a part has been made possible through the aid of a grant from Research Corporation.

EXPERIMENTS INVITED FOR TAYLOR MEMORIAL LABORATORY PHYSICS

The American Association of Physics Teachers is undertaking the production of a book of "Advanced Undergraduate Experiments in Physics," as a memorial to the late Lloyd William Taylor. The material is being supplied by the teachers of such laboratory courses; some 100 physicists have contributed experiments and suggestions. In spite of this fine response, there may be many other interesting and illuminating experiments yet to be contributed, and these experiments also should be included in this book, to give them wider circulation and thereby to enrich the instruction in advanced physics courses. Every effort is being made to obtain them.

Although the primary responsibility for this book belongs to A. A. P. I. members, contributions are cordially invited from all physicists and from colleagues in other sciences, outside the United States as well as inside. All fields of physics are represented. Informally written notes, or laboratory instructions as used by students, are quite satisfactory, since the editors must put all material into publishable form. To be of use these experiments must reach the editors not later than March 1, 1955. They may be sent to T. B. Brown, The George Washington University, Washington, D. C., or to the appropriate editor. Sections and editors are: Mechanics: R. H. Bacon, 405 Bedford Road, Pleasantville, New York. Heat: R. L. Weber, Pennsylvania State University, State College, Pennsylvania. Acoustics: L. R. Weber, Colorado State College, Fort Collins, Colorado. Electricity and Magnetism, Electronics: M. C. Harrington, Drew University, Madison, New Jersey. Optics: H. A. Nye, Cornell University Aeronautical Laboratory, Buffalo, New York. Atomic Physics and Spectra: S. C. Brown, Massachusetts Institute of Technology, Cambridge, Massachusetts. Radioactivity and Nuclear Physics: R. R. Palmer, Beloit College, Beloit, Wisconsin.

THE SOLUBILITY PRODUCT: A PROPORTIONALITY CONSTANT

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THE solubility product constant, K_{sp}, is usually developed in the textbooks on introductory qualitative analysis from the standpoint of equilibrium. Most teachers then run into the fact that students get rather baffled by the ignoring of the concentration of the solid phase. This disregard for the total amount of solid is always explained properly as being due to the building up of crystals in which the reactive part of the solid is only at the surface. The author's experience has been that too great a proportion of students still try to work in the solid phase concentration.

For several years the author has tried to develop the solubility relationships from the graphical approach, since his classes consist entirely of engineers, who can use this approach later in treatment of data. Starting with AgCl (graph 1 in the figure), it is shown that there will be a certain concentration of Ag in any solution of $AgNO_3$ (point A). It is then pointed out that the addition of Cl^- will not result in formation of a precipitate until point B is reached. Repeating the process, starting with a solution of $AgNO_3$ half the original concentration, a point C is obtained which represents a Cl^- concentration which is *not* necessarily double the Cl^- concentration found in the first case. Continuing this process, the curve of graph 1 is obtained.

The attention of the class is now called to the fact that the curve is *apparently* one of the type (xy = constant). If, therefore, $[Ag^+]$ is plotted against $1/[Cl^-]$, a straight line should result, as in graph 2 in the figure. *Since* a straight line has been produced by such a plot, it must be that the correct equation relating the concentration of Ag^+ to Cl^- is

$$[Ag^+]\,[Cl^-] = K$$

K is the slope of the line produced in graph 2, and can be used to calculate how much of either of these ions can exist in the presence of a given amount of the other if the solution is saturated with AgCl. The "if" in the last sentence returns us to graph 1. A saturated solution of AgCl is represented by the curve of graph 1. Below the curve there is unsaturation. Above the curve there is supersaturation. *Only* at point D (the equivalence point) is $[Ag^+]$ equal to $[Cl^-]$.

If the same procedure is carried out with $PbCl_2$, a curve similar in appearance to that of graph 1 is produced, but on plotting $[Pb^{++}]$ against $1/[Cl^-]$, it is found that a straight line does not result (graph 3, curve A). We now return to the difference between the formulas AgCl and $PbCl_2$. From the ionic standpoint the difference is in the number of Cl^- per cation in the formula. From the mathematical standpoint, however, we realize that a doubling of the Cl^- concentration will only shift the curve to one side, and not straighten it. Raising to a power will be a way of straightening the curve, so a new plot of $[Pb^{++}]$ against $1/[Cl^-]^2$ is made and results in the straight line B of graph 3. The equivalence point is the only place at which $[Pb^{++}]$ is half the $[Cl^-]$.

Similar graphical methods are carried out by the student to determine values of K_{sp} for more complex compounds. This leads to the problem of an unknown A_xB_y to determine values of x and y and K. The students now find out about log-log plots and about log-log paper, about both of which they seem to be ignorant, in spite of being sophomores.

From his previous work it now has become apparent to the student that the form of the ion product is set up by simply taking the formula, putting in brackets to represent concentrations in moles per liter, and "moving the subscripts upstairs." So the correct form of the ion product expression for A_xB_y becomes

$$[A^{+y}]^x\,[B^{-x}]^y = K$$

Taking logarithms

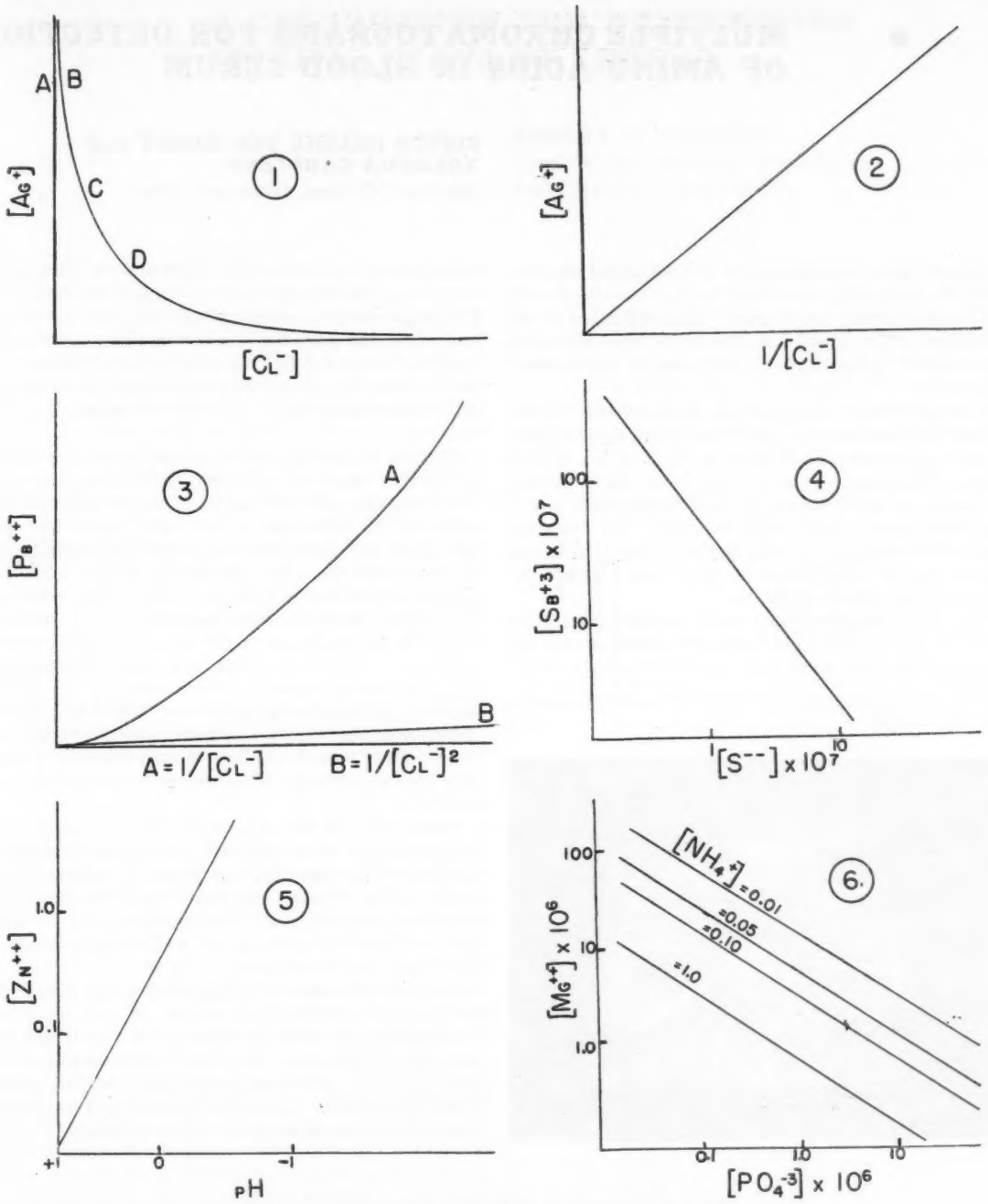
$$x \log A^{+y} + y \log B^{-x} = \log K$$

When $\log A^{+y}$ is plotted against $\log B^{-x}$ the slope is $-y/x$. The result of such a plot is shown in graph 4. Since x and y must be small whole numbers for the solubility product expression to apply, it is fairly simple to figure out their values once the ratio is determined. Once this is done, K can easily be determined. Graph 4 is for the compound Sb_2S_3.

The effect of pH on solubility can also be illustrated graphically, as in graph 5, which is for ZnS. Error due to low pH can be observed from the graph.

The log-log plot returns with graph 6, when the effect of varying more than one component shows up. For engineers such a graph can be used as an important precursor to work to be done in later courses.

The author has tried to illustrate a slightly different approach to the presentation of solubilities in salt solutions and the calculations involved in them. He believes that for engineers this approach has certain advantages over the traditional one and avoids the traps set up by doubling concentrations when the initial approach is from pure salt solutions. Since there are students who get confused by either method and it is impossible to remove previous knowledge and start over, teachers cannot be quite sure which is better.



Graphical Presentation of the Relationships between Anions and Cations

1. Variation of silver ion concentration with chloride ion concentration
2. Variation of silver ion concentration with the reciprocal of the chloride ion concentration
3. Variation of lead ion concentration with the reciprocal of the chloride ion concentration
4. Variation of antimony ion concentration with sulfide ion concentration using a log-log graph
5. Variation of zinc ion concentration with pH in the presence of sulfide ion. Semilog graph
6. Interrelationships between $[Mg^{++}]$, $[PO_4^{-3}]$, and $[NH_4^+]$, log-log scale

MULTIPLE CHROMATOGRAMS FOR DETECTION OF AMINO ACIDS IN BLOOD SERUM

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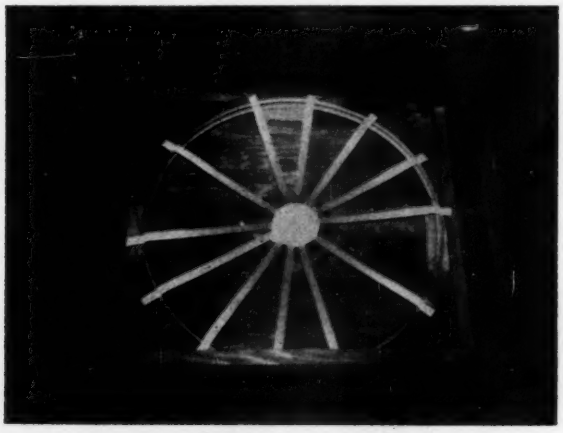
A SIMPLE piece of apparatus was constructed whereby 2 to 16 chromatograms could be run simultaneously and under identical conditions. A modification of the technique of Giri, *et al.*[1] was used in the separation and detection of amino acids in pathological and normal blood sera.

A metal circular rim of 50-cm. diameter and 2.5-cm. height was used as the support for one to eight lengths of one-centimeter-wide Whatman No. 1 or No. 4 filter paper. The 0.5-cm. groove at the outer top of the rim contained a heavy piece of cord underneath which the filter paper strips were fastened. By inserting short pieces of cord at right angles to the rim, it was easy to pull the cord out of the groove and anchor the strips of filter paper beneath it.

The strips of filter paper were punched simultaneously in their centers and fastened radially across the frame so that the holes were mounted exactly above one another. A semicircular piece of 9-cm. filter paper was cut at the straight edge to form a brush-like tip. The paper was then rolled cylindrically into a wick and inserted in the punched hole of the filter paper strips. The brush edge of the wick was immersed about one centimeter into the phenol carrier solution contained in a small evaporating dish. (See the accompanying illustration.)

[1] GIRI, KRISHNAMURTHY, AND VENKITASUBRAMANIAN, *Lancet*, **263**, 562–3 (1952).



Samples of pathological or normal sera were applied in 0.5-mm. spots at a 2.5-cm. radius from the wick. The apparatus allowed the use of two samples on each strip, one on either side of the wick. After the spots had dried, the apparatus was placed horizontally in a 55-cm. square box, approximately 15 cm. high, furnished with a removable glass top. For Whatman No. 4 filter paper the time required for the carrier to travel the 22-cm. length of the strip was approximately six hours. The rim and mounted strips were removed from the box and dried in a forced-draft hood. Spraying with the developing agent was carried out directly on the mounted strips. In some cases the strips were removed and placed adjacent to each other on a paper tray before spraying. The strips were dried in an oven at 60°C.

Advantages of this apparatus are: (1) large numbers of samples of sera may be chromatographed simultaneously; (2) identical conditions of separating the amino acids, drying, and developing the chromatograms are insured; and (3) comparison may be made with controls of pure amino acid samples analyzed under identical conditions.

A miniature model of this apparatus was used in the preliminary analysis of the serum. A wire frame was constructed and the filter paper strips were folded over the edge of the wire. The same wick technique was used and the entire apparatus was inserted into an empty desiccator. Under these conditions an approximate analysis could be made within an hour.

A CALORIMETER FOR DETERMINING SPECIFIC HEATS OF LIQUIDS

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THE usual procedure for determining the specific heat of a liquid involves adding a known quantity of heat to the liquid and measuring the corresponding rise in temperature. The heat is customarily added as a known amount of electrical energy to a heating coil immersed in the liquid.[1] From a comparison of the potential across the heater and across a standard resistance in series with the heater, together with the time of current flow, the amount of heat added can be calculated. While the electrical method is capable of considerable accuracy, the need for such accessory equipment as storage cells, a potentiometer, and a timing device considerably complicates what can otherwise be a simple apparatus. The present paper describes a calorimeter which circumvents these difficulties by employing a chemical reaction as the heat source.

APPARATUS

The "chemical heater" employed is shown in Figure 1. The heater is constructed from thin-walled Pyrex glass tubing. A known volume (5 milliliters) of 2 *N* aqueous H_2SO_4 is pipetted through tube *A* into tube *D*. In the same manner, 5 ml. of 2 *N* NaOH is pipetted into tube *E*, through *B*. The liquids are normally kept separate by air trapped in tube *C*. Tube *C* extends from the bottom of *D* up the side and through one wall of *E*, and extends nearly to the bottom of *E*. By attaching a rubber bulb from a medicine dropper to *A* and compressing, the air in *C* is expelled and part of the sulfuric acid solution is transferred to *E*. By alternately compressing and releasing the bulb a number of times, the two liquids are effectively mixed. The relation of the heater to the rest of the calorimeter is shown in Figure 2. The calorimeter is constructed almost entirely of glass. The Dewar flask was purchased from the Scientific Glass Company of Bloomfield, New Jersey. It comes equipped with metal stand and S/T 45/50 joint. The combination top and stirrer tube shown in relation to the rest of the apparatus in Figure 2, and separately in Figure 1, is constructed from an inner 45/50 Pyrex joint and Pyrex tubing. For additional thermal insulation, the entire apparatus is placed inside a tube of Micarta,[2] closed at one end, and the top packed with fine glass wool as shown in Figure 2. About 200 milliliters of liquid sample is used. With the Dewar flask shown, this is sufficient to cover tubes *D* and *E* of the heater. Stirring is accomplished by a moderate flow of nitrogen, or, for inert liquids, compressed air, through the stirring tube. For volatile liquids it is usually necessary to presaturate the gas by passing it through a bubbler con-

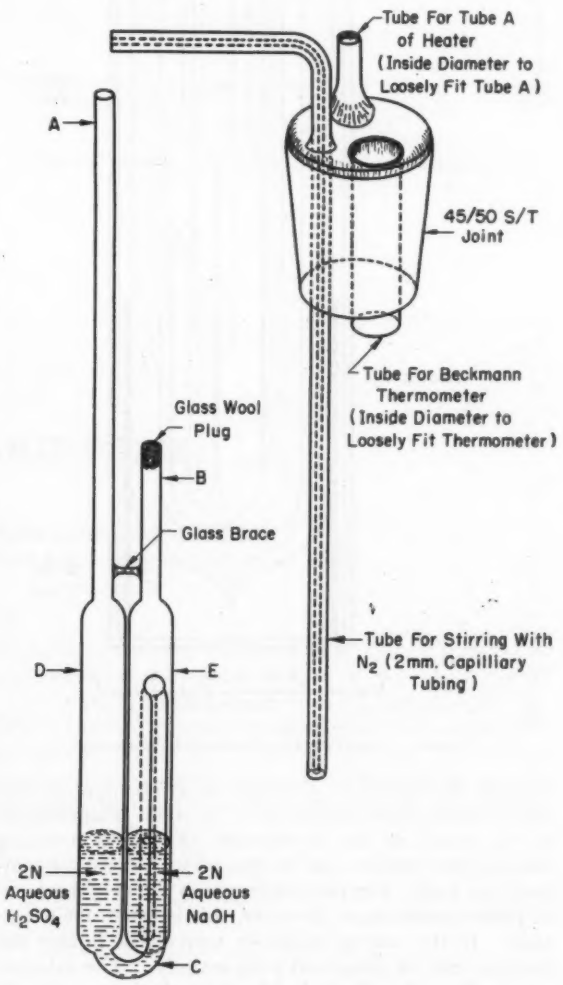

Figure 1. Chemical Heater and Top for Calorimeter

[1] WEISSBERGER, A., "Physical Methods of Organic Chemistry," 2nd ed., Interscience Publishers, Inc., New York, 1949, Vol. I, p. 773.

[2] A phenolic resin laminate. Any other durable insulating material would be suitable.

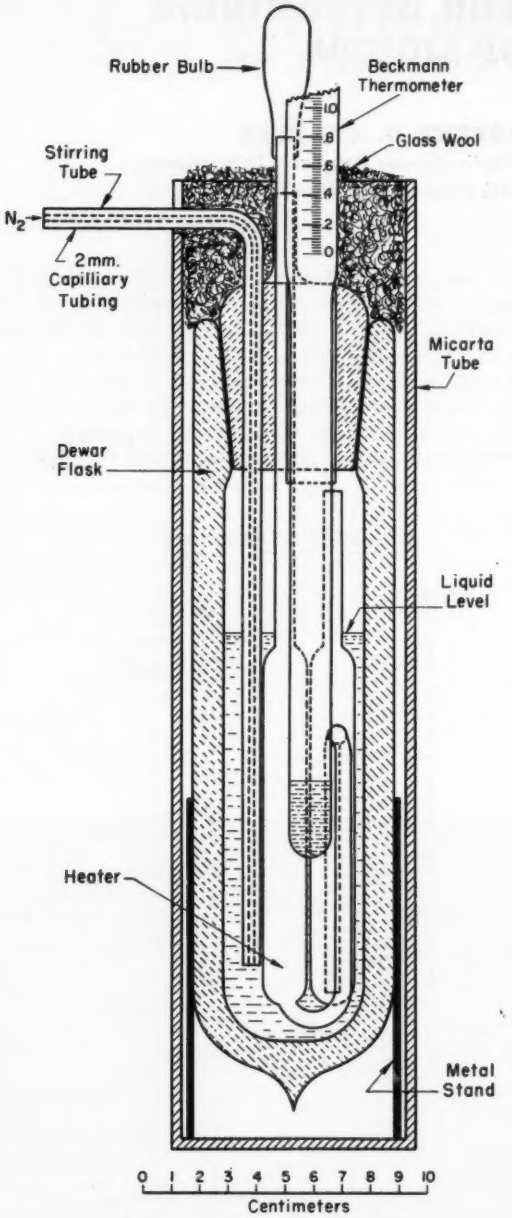

Figure 2. Cross Section of Assembled Calorimeter

taining the liquid in question at approximately the same temperature (±3 or 4°C. at room temperature) as the liquid in the calorimeter. For most accurate results, the bubbler can be placed in a constant-temperature bath. For measurements in the neighborhood of room temperature, however, this is often not necessary. In the case of relatively nonvolatile liquids the bubbler can be dispensed with entirely. The calorimeter, as here described, has been used almost entirely for measurements in the neighborhood of room temperature. There is no reason, however, why, with suitable precaution, it cannot be used at either higher or lower temperatures, although the accuracy will generally be lower because of increased heat leakage. At temperatures much above or below room temperatures, it becomes increasingly important to preheat or precool the stirring gas by passing it through a coil and/or a gas bubbler in a bath maintained at the approximate temperature of the determination. Temperature in the calorimeter is measured by means of an ordinary Beckmann thermometer which can be read directly to 0.01°C. and estimated to ±0.001°C.

PROCEDURE

The general procedure for a determination is as follows: Approximately 200 milliliters of the liquid to be measured is adjusted to the desired temperature and weighed (to the nearest 0.1 gram) into the Dewar. Acid and base are pipetted into the heater, which is then placed in the Dewar. A small plug of glass wool is placed in tube *B* (Figure 1) to prevent the reacting liquids from splashing into the liquid being measured in the Dewar. The Dewar is placed in the Micarta tube and the apparatus assembled as shown in Figure 2. Stirring is begun and the apparatus allowed to come to thermal equilibrium. Fifteen minutes is generally sufficient. Temperature-time readings are then taken at five-minute intervals for the next fifteen minutes. The heater is activated by alternately compressing and releasing the rubber bulb. It is well to do this fifteen or twenty times to ensure complete mixing. Temperature-time readings are then taken at five-minute intervals until the difference between successive readings becomes constant. The entire determination takes about 45 minutes. The procedure for calibration and for measuring a liquid of unknown specific heat is the same, except that in the former case a liquid of known specific heat is used. Distilled water is quite satisfactory for this purpose.

CALCULATIONS

It is necessary to calibrate the calorimeter, since part of the heat released by the heater is absorbed by the calorimeter proper rather than completely by the liquid being measured.

$$H = (\text{sp. ht.}_{\text{liq.}})(w_{\text{liq.}})\Delta t + (\text{ht. cap.}_{\text{cal.}})\Delta t$$

where H is the heat released by the chemical reaction, sp. $\text{ht.}_{\text{liq.}}$ is the specific heat of the unknown or of the calibrating liquid, $w_{\text{liq.}}$ is the weight of the liquid in grams, Δt is the temperature rise, and $\text{ht. cap.}_{\text{cal.}}$ is the heat capacity of the calorimeter. The value for Δt is obtained by plotting temperature readings against time and extrapolating the fore-and-after periods to the time the heater is activated.[3] This is also easily done arithmetically from the average rate of temperature change with time in the fore-and-after periods. The heat capacity of the calorimeter is evaluated by calibrating with water or other liquid for which the

[3] WEISSBERGER, A., *op. cit.*, p. 744.

term sp. ht.$_{liq.}$ is known. The specific heat of an unknown liquid is then given by

$$\text{sp. ht.}_{liq.} = \frac{H - (\text{ht. cap.}_{cal.})\Delta t}{(w_{liq.})\Delta t}$$

For the reaction of 5 ml. of exactly 2 N H_2SO_4 with 5 ml. 2 N NaOH, H is calculated to be 165 calories at 25°C.[4]

ACCURACY OF MEASUREMENTS

Figure 3 illustrates the accuracy to be expected with this type of apparatus. The solid line represents values calculated from data given in the "International Critical Tables."[5] The experimental points represent a typical series of single determinations obtained at 25 ± 1°C. with the calorimeter here described, using water as the calibrating liquid. The deviations average about ±0.01 cal./gram/°C. Individual values are generally reproducible to about ±0.02 cal./gram/°C., with an average deviation from the mean of ±0.01 cal./gram/°C. for a series of such runs.

[4] ROSSINI, F. D., ET AL., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500 (1952).

[5] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1929, Vol. V, p. 116.

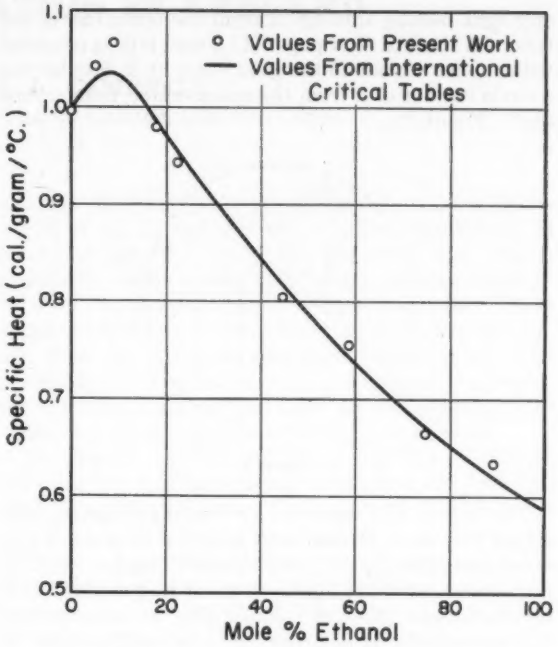

Figure 3. Specific Heats of Ethanol-Water Mixtures at 25°C.

A STUDENT POLARIMETER

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POLARIMETRY as an analytical technique is, unfortunately, rarely, if ever, used in courses prior to junior- or senior-year physical chemistry. The fundamental manipulations and the theoretical background required for successful use of the polarimeter are not the basis for the existence of this situation. Colorimetric procedures, which are no more involved than polarimetric ones, are commonly employed. It appears that the reason for ignoring and neglecting polarimetry in analytical or even freshman courses is that the instruments are so expensive. The purpose of this paper is to describe the construction and use of a crude polarimeter that would be suitable for use in these earlier courses.

Construction. The apparatus uses pieces of polaroid film as the polarizer and analyzer. The material distributed by theaters exhibiting 3-D motion pictures is well suited for this application.

An ordinary microscope slide is cut in half and each half is sealed to the ends of a condenser jacket with rubber cement (Figure 1). This serves as the polarimeter sample tube. At end A, which is the eyepiece end, a slip of polaroid film is fastened with a paper clip to filter

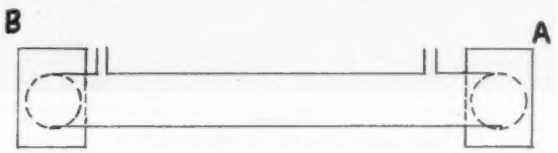

Figure 1

any light passing through A from the other end of the tube. A sheet of filter paper (11.5 cm.) is then mounted with rubber cement to the glass cover at B, first having a circle cut out of it from the exact center, using a cork borer (Figure 2).

Figure 2

The tube is now mounted by cradling it horizontally across two buret clamps each attached to a small ring stand and pointing the setup toward a window or other convenient source of light. A third ring stand, which carries another piece of polaroid film, is set up so that this second strip of polaroid film is in the direct line of sight leading from A, through the polarimeter tube, and through B to the light source. A pencil is also fixed to this ring stand so that its point just touches the edge of the filter paper on the tube at B.

Manipulation. With the empty tube as originally assembled, the entire tube is rotated about its long axis while the operator looks through the apparatus at the light source. Figure 3 shows the equipment ready for use. As the tube is rotated about the point of maximum extinction a chromatic phenomenon appears. The extinction point is taken as the position of the tube when the deepest blue shade is observed. At this time the filter paper attached to B is pressed against the pencil point to leave a mark on the paper.

The entire tube is now removed from the supports carefully, so as not to move the ring stands or to disturb the position of the filter paper or either piece of polaroid.

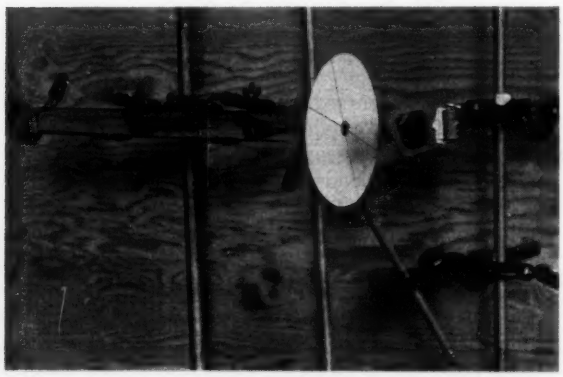

Figure 3

The solution to be measured for optical rotatory power is now introduced into the tube. This is conveniently done by attaching short lengths of rubber tubing to the water inlet and outlet tubes of the condenser jacket and sucking on one tube while the other dips into the solution. When the tube is full, the inlet tube is pinched. The sucking tube is removed and is replaced by a rubber bulb from a medicine dropper. Another such bulb is used to replace the other length of rubber tubing. Care must be taken, of course, to exclude any air bubbles from the polarimeter tube. The filled tube is now replaced in the original position on the supports. A new reading is taken by rotating the tube while looking through the eyepiece and a new pencil mark made on the filter paper.

A second sheet of filter paper, the record sheet, is now superimposed upon the one attached at B and the pencil marks are transferred to it.

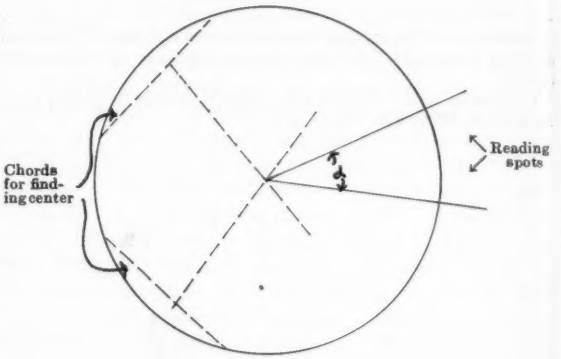

Figure 4

Calculation. The center of the record sheet is found by constructing the intersection point of perpendicular bisectors of two chords drawn on the paper. Lines joining the center and the two recorded points are drawn and the angle of rotation between them is measured with a protractor. A typical record sheet is shown in Figure 4.

Results. When a tube length of 312 cm. was used to measure the rotation of sucrose solutions varying from 5 per cent to 12 per cent at room temperature (*ca.* 25°C.) values for specific rotation ranged within 66.2° ± 1.4°. These are quite consistent results, considering the crudity of the equipment. To check the validity of the data, readings were taken on these same solutions using a Kern Polarimeter and a value of 66.0° was obtained. The precision of the apparatus may be taken to be in the order of magnitude of one degree of rotation corresponding to a variation in specific rotation values for a 5 per cent solution of about 0.65°.

CHEMICAL EDUCATION IN ENGLAND

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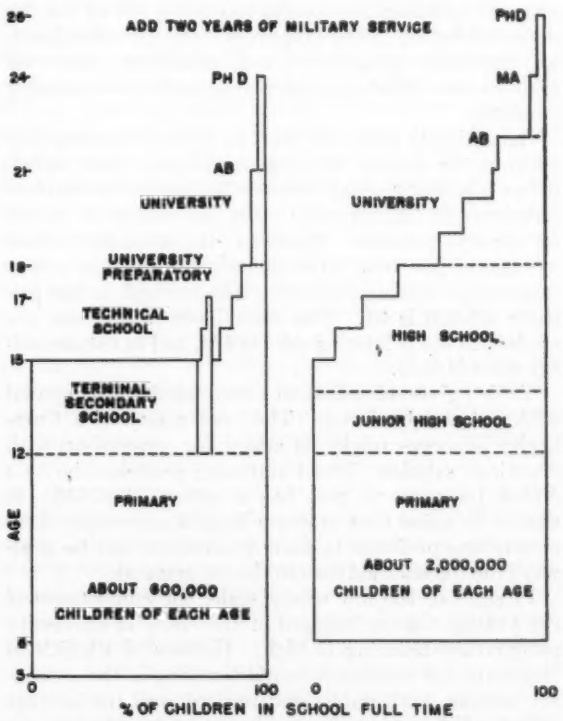
DURING the academic year 1952–53 I spent some ten months in England, mainly at Cambridge University on a fellowship from the Fund for the Advancement of Education. The experience was hardly unique, the current flow of chemists being as great as it is between the two countries, but some of the notes on the educational system may be of interest.

One of the great present complaints of chemists in the United States concerns the preparation and education of new chemists both as to quality and as to quantity. Yet one can scarcely be in England more than a few days before he runs into the claim, often made by a visiting American, that the English student from age 18 on is at least two years ahead of his American contemporary in preparation. Furthermore, chemistry is one of the fields of study most sought after by the gifted student. Only modern languages, history, and medicine rank ahead of chemistry in number of state scholarship holders in the universities. About nine per cent of these scholarship people are in chemistry. Whence comes this apparently roseate situation? Can we attain a similar one? Imagine that 10 per cent of new high-school graduates, age 18, were able to enter the junior year of the typical American University chemistry curriculum and do work of scholarship caliber!

Before we can even attempt to prescribe toward such a situation a brief outline of the English system is in order. The figure[1] lists the general steps in the education of an English child in comparison with that of a similar American. In America the child enters upon his primary education at six, goes to junior high school at 12, and senior high school at 14. A majority graduate from high school at 18 and almost half of all 18-year-olds continue school after graduation from high school. About half of these graduate from college with a bachelor's degree, and a few per cent then proceed to a higher degree.

An English child typically begins primary school at five. At age 11, if his IQ is above approximately 105, he takes an examination, which determines whether his further education will prepare him for the university or not. Some 25 per cent of children age 12 are selected to enter secondary grammar schools from which later entry to the universities is possible, some five per cent go to technical schools, and the rest enter schools designed to give an education terminating at age 15. Seventy per cent of English children leave school at age 15 and only about 10 per cent are still in school at age 17. About five per cent of all youth eventually enter a university, either at about age 18 or, after two years of army service, at about 20. Three years are spent at the university as an undergraduate, and three more if a doctor's degree is obtained. The percentage of English obtaining advanced degrees in the sciences is almost the same as the percentage of Americans obtaining a doctor's degree in science.

The figure summarizes the probability of school attendance as a function of age in England and America. The data vary, of course, from year to year, but the figure is a schematic representation of the general comparisons. Two main differences are apparent: (1) The English system selects the exceptional students at an early age and carries their education along separate from the rest. (2) The American system includes a very much larger percentage of the age group from 15 to 22. The two systems are comparable in percentage of students below age 15 and above the college graduation level.



School Attendance in England (*Left*) and America (*Right*)

[1] The reports of the Anglo-American Council on Productivity are an excellent source of comparative data. They may be obtained from the Council, 2 Park Avenue, New York 16, New York. A catalogue of the some 60 reports available and their prices will be sent on request.

TABLE 1

Age	Average salary: Grammar school	Industry
32	$1820	$2810
35	1970	3480
46	2030	4630
	(Special responsibility may add $200–$300)	

It could be logically deduced from the figure that it is in secondary education and college education that one can find the most interesting differences between English and American education and it is to these levels that we shall principally limit ourselves.

Staffing and Maintaining the Schools. It should be clear from the figure that the English staffing and maintenance situation might be expected to be less severe than our own. After all, a much smaller percentage of the population is in school. Actually the situation seems quite comparable. The newspapers and the official reports are full of accounts of teacher shortages, insufficient buildings and space, inadequate equipment, and minuscule salaries in the school system. English parents seem to have reacted after the war much as did American parents, and the younger population is now needing schools in ever increasing numbers. Split days are common and many emergency facilities are pressed into use even as with us. Unfortunately, building in England is much more difficult than here and new buildings are coming too slowly for all but the most hidebound of the taxpayers. On the other hand, an ambitious program is well underway, and well planned new buildings and playgrounds are becoming available.

Immediately after the war an extensive emergency program for teacher training was begun. Just ended, it has provided enough teachers to prevent a complete imbalance in teacher-pupil ratio, but classes of 40 and up are still common. However, the secondary-school average of just over 20 students per teacher is a very respectable accomplishment. The average in the primary schools is 31. The annual per capita cost per student in the primary grades is $73, and in the secondary schools $123.

Table 1 gives some data on school salaries as compared with industrial salaries. The base salary of a Cambridge professor might be added for comparison with American salaries. The Cambridge professor, be he a Nobel Laureate or not, has a salary of $5600. It should be noted that in every English university there is only one professor in each department and he is always the top-salaried man in the department.

In spite of the low salary scale, the competence of the average teacher engaged in university or university preparatory teaching is high. Holders of Ph.D.'s in chemistry are commonly found teaching in the secondary schools, both public and private, and the average caliber of the university teacher is higher than in the United States.

Public School and Private School. Very few secondary schools were started in England between the middle of the seventeenth century and the middle of the nineteenth century. Thus, most present-day schools stem from ancient foundations or are of rather recent origin. This difference has had a great effect on English education in the past but the differentiation is beginning to disappear. Practically all of the ancient foundations are not tax-supported. They are what we call private schools. Many have been top-flight schools for hundreds of years. Many other private schools of outstanding reputation are of recent origin, and an increasing number of tax-supported institutions, or public schools in our words, are of the highest rank in preparing students for the universities. Manchester Grammar School has an outstanding record, producing more successful candidates for university scholarships at Cambridge and Oxford in 1952–53 than any other school. Each year slightly more than half these scholarships go to youths whose education has been in private schools and about half to youths from schools receiving some or all of their support from taxes. Since less than half of the university entrants are educated in the private schools it is clear that the private-school students get a slightly better share of the awards than relative numbers would predict.

The private schools have become the center of a mild controversy during recent years and considerable talk has been directed at broadening their base of admission, until it depends less on economic or social status. The 1944 Report of the Committee on Public Schools [2] (we would say private schools) contained the following statement: "We realize the possibility that just as some parents now send their sons to Public Schools, partly, perhaps mainly, for the sake of social or economic advantage, so our proposals may attract some other parents who are interested mainly in the same narrow advantages.... It has been very freely stated to us that Public School men generally show a lack of sympathy with, or even understanding of the lives and difficulties of the other classes in society, from which they are said to be wholly segregated, and particularly of those engaged in manual and technical work; and that they are out of touch with social realities and incapable of grasping modern social conditions." It seems likely that an ever increasing number of scholarships will be available to these schools and that they will represent, in their student bodies, increasingly varied economic and social backgrounds.

The transition has occurred already in the universities, all of which are largely tax-supported, and it is commonly agreed that no competent student is any longer denied university admission because of economic need or social background. On the contrary, univer-

[2] The annual reports of the Ministry of Education cover the field of public education thoroughly and are voluminously documented. Prices and copies available from Her Majesty's Stationery Office, P. O. Box 569, London S.E.1. "Education 1900–1950" is a valuable review (price 7*s.* 6*d.*) available from this office. "The Public Schools and the General Educational System" from the same office discusses the role of boarding schools.

sity and government scholarships are now the rule rather than the exception at all universities. At Oxford and Cambridge more than 85 per cent of the undergraduates hold some kind of scholarship. In fact, almost two hundred state scholarship holders were unable to find university places in 1952 owing to tight competition for the available places. There are no private colleges as we know them, yet there is no governmental interference with higher education.

The "old school tie" has much less effect now than fifty years ago. Only some 6000 places for boys and 2000 for girls are open annually in the private schools. As the opportunities for education are more widely available to the 600,000 children in each age group, the overwhelming dominance of the private school will wane, though it certainly will continue important.

Scholarships. As we have just indicated, scholarships are available in England on a scale seldom dreamed of in this country. In 1951–52 18,500 new students entered English universities. Of these, 10,300 had awards from their local governments, 2000 had awards from the national government, 1500 had awards from a university (and 700 of these awards were supplemented by government grants), and 2000 were overseas students ineligible for awards. The remaining 2700 students were able to afford an education without scholarship aid. Eighty-four per cent of the eligible students had scholarships of some type.

Practically all these awards are highly competitive. Three times as many candidates sit for the state awards as can be successful, and the ratio for the university awards is even higher. Nor is the caliber of the examination low. The university scholarship examinations would be passed successfully by only a small fraction of the entering juniors in a typical American chemistry department. Some random questions from the Cambridge College Examinations [3] follow.

(1) An organic acid, A, on treatment with phosphorus pentachloride yielded a substance, B, which contained 78.0 per cent of chlorine, and had a molecular weight of 182. B when treated with dilute sodium carbonate solution yielded a substance C, which when crystallized and heated with soda lime produced a volatile liquid D, which when heated with aniline and sodium hydroxide solution yielded a substance possessing a highly offensive odor. Assign a formula to the original acid, and explain the course of the reactions involved.

(2) Discuss the factors affecting the electrical conductivity of solutions of electrolytes. The equivalent conductivity at 25 °C. of a centinormal solution of acetic acid is 16.3 units. If the equivalent conductivities at infinite dilution and the same temperature, of sodium acetate, hydrochloric acid, and sodium chloride in aqueous solution are 91.0, 426.1, and 126.4 units respectively, calculate (*a*) the acid dissociation constant of acetic acid and (*b*) the pH of centinormal acetic acid. What is the conventional unit of equivalent conductivity?

(3) Four general papers on subjects like these. (*a*) "L'état, c'est le monsieur derrière le guichet." (*b*) Discuss the case for a technological University for Great Britain. (*c*) Would proportional representation destroy the two-party system in English politics? (*d*) "Increased productivity is a euphemism for harder work." (*e*) Middle Eastern nationalism.

[3] Examination papers of the Cambridge and Oxford colleges may be obtained from the respective University Presses.

Perhaps it should be added that the examinations are all multiple-choice.

Education for Men and Women. There are some 85,000 students in the 23 English universities, of whom 19,500 are women. The numbers of men and women at Cambridge and Oxford, the ancient universities, give even higher ratios: 7200 to 710 and 6122 to 1085, respectively. We have already pointed out that the ratio in the private secondary schools is three to one. On the other hand, the girls do not leave secondary school any sooner than the boys and there are just as many girls in the college preparatory sequence as there are boys. As a result, there is only about one-fourth the chance for an eligible girl to get into a university as for an eligible boy. Although the government scholarships are granted on a slightly more favorable ratio for the women (three to one) it is clear that the intellectual level of women in English universities must be higher than that of the men.

The generally higher caliber of the women is well recognized by all but the hardiest of bachelors, yet one hears over and over the statement that the best students, the ones with the most scholarly zest, are always men. Professors of many years' experience do not recall many instances of really outstanding women scholars compared to the men. This is not true only in science. Similar statements are heard in other fields such as history and economics. My own experience in America does not jibe with this observation and I leave it to someone more venturesome than myself to prove whether the difference lies in the teachers, the girls, or the civilizations. Lest I be accused of avoiding the issue completely, I will state that our own experience of having two daughters in a first rate English private boarding school would attribute the difference to the general culture. It seemed clear to us that discipline was much tighter for the girls than for the boys in England and certainly than for the girls in the States. Our own school was beautifully run and much more free than others, yet there was clearly less room for initiative, unbounded quest of new ideas, and general freedom than would seem ideal.

No comment on English education can omit mention of the almost complete absence of coeducation in the secondary schools. Almost none of the private schools are coeducational and even the public schools are divided into boys' and girls' schools with separate staffs, curricula, and playgrounds. The feeling is practically unanimous that the segregated school gives conditions more conducive to work and that better scholarship is clearly achieved. It is also rather generally admitted that social development is markedly slower under these conditions and that social poise, in mixed company particularly, is not fostered.

The Ancient Universities. Oxford and Cambridge occupy a place unmatched among the English universities. Each claims to be the older and the official government statement waives the issue by listing both as "existing from time out of mind." They are distinguished from the other 21 new universities by the

title "Ancient Universities." Each recognizes the advanced degrees granted by the other but not the degrees granted by any other university in England. Conversely, the other 21 universities are known as the provincial universities, or the "red-brick" universities. In order to overcome somewhat the academic furor that would result if a professor had no advanced degree, both Oxford and Cambridge automatically confer master's degrees on new faculty members not fortunate enough to have had the advantage of being educated at either ancient university. It is, therefore, unsafe to use the title "Doctor" even for the most distinguished member of the faculty until you have investigated to see whether the title has official local standing. ("Professor" must, of course, be used with even greater care.)

Until the nineteenth century these were the only English universities. They produced not only the outstanding English scholars, but *all* English scholars. It came as a great surprise, indeed, to be told by a Cambridge professor that the high academic standards now pertaining at each institution are less than forty years old, and that it is only in the last ten years that one had to be a good student to graduate. Even now the graduation requirements are only two: sleep within one's college a set number of nights each term, and pass two examinations—Part I at the end of the first or second year depending on the university, and Part II at the end of three years. The caliber of work on the examinations determines whether the scholar obtains a first, second (class (1) or (2)), third, or pass degree. Almost no failures are reported any more and very few obtain only a pass degree. The distribution of examination results at Cambridge in 1952 is listed in Table 2.

Direct comparison with our universities is not feasible, but it is safe to say that there is no American university, or English either for that matter, which equals these two ancient universities in general intellectual ability and gift of students. Without much question the majority of English students still place Cambridge or Oxford as their first choice. About a third of all the holders of state scholarships go either to Oxford or Cambridge and the intimation is rather strong that it is the top third. A University Scholarship at either place is the highest academic goal of most secondary-school students. Any university can afford to keep some of its ancient crochets as long as its product is so rare.

Yet it would be a mistake to leave the impression that each undergraduate borders on genius or that each graduate student skirts omniscience. I well remember walking into a supervision class to hear a physics student say, "Oh, I didn't know the volume of a sphere was equal to four-thirds pi r cubed." Then there was the graduate student who argued insistently that a ship could be driven into the teeth of a gale if one mounted a windmill on it and coupled it to the propeller. But the level of graduate students does equal any American school and the undergraduate level passes anything we have.

When one enters either ancient university he does so through application to one of the constituent colleges, not through the university itself. This leads to the unusual situation that certain of the more famous colleges have long waiting lists whereas others just barely fill their quota. The colleges are essentially living places, but each college also has its own faculty which it shares with the university. Thus these teachers, at least at Cambridge, do all their lecturing in the university, where they are available to all comers. Their own students are, however, members of their own college. Members of other colleges do not, in general, confer with the lecturer, but with the man on their college staff in the same general field. A combination of reputation of staff and history of each college leads to the uneven crowding of the application lists even though the same university work is open to all.

It is, perhaps, the residential nature of the two ancient universities as centered in the colleges which most sets these two schools apart from others. The concomitant intimacy of both student and faculty groups gives a life which attracts quality and gives it room to increase. Each man, student and faculty alike, has firm professional connections and interests within the university, but he also has social contacts which cross all professions in the dining hall, the common room, and the private quarters of his college. The pleasant setting of each college in its own lovely garden and magnificently kept lawns is an added inducement to leisurely but thorough scholarship and study.

TABLE 2

	Degree						
Examination	*% first*	*% second (1)*	*% second (2)*	*% third*	*% special, etc.*	*No. of candidates*	*No. of women*
Mathematics I	38	32	...	27	3	133	13
Mathematics II	25	32	...	39	4	114	10
Classics I	20	26	28	26	...	114	9
Classics II	17	34	30	17	2	99	17
Nat. sci. II	16	25	34	24	1	248	12
Nat. sci. I	13	18	42	26	1	497	10
English II	11	35	32	21	1	129	6
Languages II	10	36	42	12	...	142	12
History II	7	40	45	7	1	239	7
Economics II	7	23	41	27	2	85	4
English I	6	15	50	26	3	172	12
History I	5	39	40	15	1	274	6
Geography I	5	25	34	31	5	85	20
Law II	5	13	40	39	3	272	1
Law I	3	15	31	42	9	91	3
Economics I	3	12	37	43	5	152	7
Geography II	...	36	40	23	1	66	22

Courses and Curricula. The secondary grammar-school curriculum is both broader and deeper than that in most of our high schools. Foreign languages and elementary mathematics are begun at age 12. By age 16 most of the formal courses of what Americans call a liberal education have been passed. The last two years of secondary school (the sixth form) are spent concentrating on a chosen profession, *e. g.*, chemistry for the chemist. Some other course work is carried, perhaps not even related to science, but much of liberal education is not included in any formal course. The presumption is that the student will read literature for himself, that he will travel during vacations and study as he travels, that religion is learned by practice, and that government and international affairs are a part of each man's knowledge to be discussed and kept in view by use of the excellent radio, press, and television coverage available. The sixth-formers are given considerable responsibility around the school as prefects, bedroom leaders, and school officers. In the private schools particularly, great emphasis is laid on games, perhaps a third of the boy's time being devoted to team sports. England has as many language accents as the United States, if not more, and it is at the private schools that *the* English accent is learned regardless of the natal locale of the scholar.

The sixth form is mostly spent preparing for university entrance and scholarship examinations. Former exams constitute much of the work of the two years and the practical laboratory exams used in past years serve as the main basis of a great deal of the laboratory work. Two years of this intensive preprofessional training result in extending each student to the limit of his capabilities. Already a member of a select group since the age of 12, the student is deliberately prepared to become a member of an even more select group in the university. The selectivity varies, of course, from school to school, though perhaps less so than in America, owing to a rather more thorough use of central government advice and to the greater homogeneity of the universities which serve as the goal.

One result of the intensive preparation of the sixth form is, effectively, an overtraining of the best students. They are not only prepared for the university, but have already covered a large part of the first year's work. Several able scholars told me that one of their problems for the first year at Cambridge was to keep from going stale, since the work had so little challenge. It is at this point that the supervisory system of individual weekly conferences between each student and his supervisor can be most useful. Unfortunately, all supervisors are not equally talented.

The lectures in the ancient universities are run on a most informal basis as far as attendance is concerned. The medical and science students generally claim that lectures are absolutely essential, but two-thirds of the nonscience students getting "firsts" at Cambridge in 1952 classed lectures as useless and attended less than three per week. Lectures are usually read and are very well delivered, but most students seem to prefer to read the professor's book and other sources rather than hear him do it for them. I personally enjoyed attending lectures very much—must be a question of habit!

No attendance is taken, no quizzes or final examinations are given, lectures stop when the lecturer has covered his chosen topic even if the term is only half over. There is never any comment from the students during the lecture, and the lecturer dons his cap and disappears from the room as soon as he has finished his day's reading. Questions are taken to the supervisor. Faculty-student relations, except between supervisor and his own students, are almost nonexistent. However, a student usually has three or four supervisors each term so that his contacts are quite sufficient to encourage a range of interest and superior guidance if needed.

Each student "reads" in only a single field as indicated in Table 2. There is a minimum of crossing over borders except in such obvious cases as a theoretical chemist who takes mathematics and physics lectures and supervisions. For a chemist to discuss economics with a lecturer, however, must require some doing. Thus, three years of intensive specialized training in the university follow the two introductory years of the secondary school. At age 21 the English A.B. candidate in chemistry has had education equivalent to that of a master's candidate in the United States.

Graduate School. The master's degree is conferred automatically by some English schools on recent graduates after a certain time interval and the payment of a fee. In other schools it is an earned degree, as the Ph.D. always is. The doctor's degree course is customarily three years, compared to four in America and is usually completed at age 24, or at 26 if the two years of national service have been included. The doctorate is generally a purely research degree and is considerably more surrounded by leisure than its American counterpart. This is inevitable if one examines the background of the two candidates in the chosen profession and makes the additional assumption that the actual attainment of the Ph.D. means roughly comparable achievement in the two countries. The American candidate has at least five years of work to do in four years.

The average English graduate student gets to the laboratory between 9:00 and 9:30 in the morning, starts his experiment, takes off half an hour for coffee about 10:30, takes an hour or more for lunch about 1:00, has half an hour to an hour for tea about 4:30, and goes home to supper at 6:00. Most do not come back to work in the evening. The faculty follows a similar schedule. To the amazement of the visiting Americans, mountains of work come from the laboratory and add luster to the English literature. I asked an English professor about this strange situation. "The trouble with you Americans," he said, "is that you work too much. You ought to take more time off to think. Saves lots of time, you know."

The time to think is so strongly thought of in the English laboratories that they are locked to all, includ-

ing the professors, at 10:00 or 10:30 every night, are shut on week ends, and closed tight for two weeks at Christmas and two more weeks in August.

Part-time Education. Part-time education, both within the regular universities and in other institutions such as technical colleges, is much more common in England than in the United States. Some 250,000 men each year obtain part-time release from their industrial jobs during the day so that they can attend technical classes of one kind or another. Relatively few of these men aspire to university degrees. Far more common a goal is a National Certificate. These Certificates are granted upon satisfactory passing of an examination which, in chemistry, is given by the Royal Institute of Chemistry. The Certificates have been an important factor in insuring high-level part-time training aimed toward easing the shortage of professionally qualified men. These certificate holders are not usually counted in comparing scientific education in our two countries, though there is little question but that many of the men attaining them have education equivalent to that of many college graduates in this country, particularly in the chosen technical field. Indeed, some of the holders do go on to take graduate degrees in a university.

The Products. Most English are convinced that their average Ph.D. is better prepared than the average American Ph.D. Most Americans would agree that he is at least as well prepared, not only in chemistry but also in the sense of a liberal education. Yet he has two years less of academic training. Where are the two lost years of the American?

The question is obscured by many answerers who neglect to distinguish between professional and liberal education, but even more by many who fail to discriminate between a system which selects the best students and extends each to his maximum and one which tends to teach "for the average." The greatest single advantage of the English system does not come in early professional training but in selectivity in students and in teaching. But the early concentration also has many advantages. Many exceptional students, given a chance to extend themselves fully, have well directed interests, particularly in the middle teens. For them the liberalizing opportunities may well be deferred. As penetration in the chosen field becomes deeper many questions rise which can only be answered by branching out. Then is a logical time for nonprofessional courses or opportunities for study. Well taught professional courses will raise so many questions outside the immediate field that the student may well not only lead himself to, but also drink deeply from, the other springs of wisdom. The test of a liberal education is the use one makes of his spare time. Why not let the spare time and the liberal education for it arise simultaneously? We now have the spare time in secondary school, whereas the student getting a "liberal education" in college is so busy that he can't enjoy it.

The lost years for us are commonly agreed to be the teens, the nothing-to-do, no homework, loose-ends age. Selectivity is a possible answer here. But it is also possible that there are other lost years involved in forcing an early liberal education when a specialized term would better fit.

If then, the English system of educating scientists is really better, how does one account for the general ascendancy of American science compared to the rest of the world? The answer seems to me to lie in the very point which is the strength of the English and Continental system—selectivity. Selectivity is not only a strength, but a vicious weakness. One of the great strengths of the American system, indeed, is the unselective nature of its education. The figure clearly shows the generally longer period of education in this country and the much larger number continuing until age 22—some three times as many as in England. It is on this group that the real strength of American education rests. We do no better job, perhaps not as good a one, on the most gifted and we take longer to do it. On those less intellectually gifted the story is different. Here are the ones who, though no geniuses, no great discoverers, no pioneers of knowledge, can make things work. They have the common touch; they are practical.

A selective system is always based on a particular criterion. Academic selection picks those who will succeed in a special way. Modern society needs these, but it also needs those on the next layer of academic ability whose talents may be greater in organization, leadership, application. The advantage of the American system is that each person is encouraged to go as far as he wishes to go. The ones who drop out do so largely for personal reasons.

Many English feel that the examination at age 11 is the great crime of modern English education. It is too selective at exactly the wrong time. But many others point out that the real waste in contemporary English education is beyond age 15, when less than one-fifth of those trained for the university can get in, because of physical limitations in the size of the university system.

The result in the field of engineering is typical. Britain produces twice as many Ph.D.'s in engineering per unit of population as does the United States. She also produces twice as many persons with training equivalent to our master's degrees in engineering. The big difference comes at the level of our bachelor's degree in engineering. Here the ratio is in the favor of America by three to one. Since the number of such candidates is greater than for the advanced degrees, America has a much larger group of men trained to a high enough degree to make a large industrial organization possible. England lacks the broad base of trained manpower necessary for mass industrialization and production.

Our aim, then, should be to maintain our mass education, even to enlarge it, but to place within the system means whereby gifted students can realize that their gifts are to be given to the full, not merely used when absolutely necessary. We might even liberalize liberal education.

"AND GLADLY TEACH"[1]

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WHEN one has the great good fortune to be singled out for such an honor as this, he is tempted to think first of his own lack of merit, next of the many others who deserve it more, and then of the many persons whose aid, counsel, and encouragement have contributed to whatever he has accomplished. One thinks of his teachers, his associates, and his administrative superiors who have guided, encouraged, and directed him. To all of the many concerned, the author wishes to express his sincere thanks and grateful appreciation.

My first and best teacher was my father. Trained in the classics at the State University of Iowa, he was a pioneer teacher in the state of Nebraska. Even amid the rigors of a frontier farm, he illustrated the pleasure of scholarship and the joys of intellectual achievement. My first teacher of chemistry was Professor H. O. Sutton of the Nebraska State Normal at Kearney, Nebraska. Able, competent, and inspiring, he started many a young man on a career in science. At the University of Nebraska Dr. Benton Dales taught me the important lesson that one who aspires to be a chemist must dedicate himself to a lifetime of study.

Professors Frankforter, Barbour, Schram, and Alexander each did much to expand my horizons and quicken my enthusiasm. Graduate school brought me under the influence of Professor J. A. Wilkinson at Iowa State College and of Professor A. W. Browne at Cornell. It has also been my great privilege to have had as associates such outstanding teachers as Frank Emerson Brown at Iowa State, Cannon Sneed at Minnesota, Edmund Burke at Montana State, and Roland Ward at Brooklyn Polytechnic. During these same years the friendly understanding and encouragement given by Dean O. M. Leland at Minnesota, President Alfred Atkinson at Montana State, and President H. S. Rogers at Brooklyn Polytechnic have contributed greatly to my work as a teacher and as a departmental administrator. Here too, I must acknowledge the counsel and support of many alumni of Brooklyn Polytechnic. There are so many names here that I dare not start the list.

THE TEACHER

The teacher is the key figure in any organization devoted to education. All other considerations must be subordinated to this one. If one has good teachers, any organization will work. However, a scheme which will give to each teacher the greatest opportunity to follow his own star is usually one that involves a vertical rather than a horizontal scheme with respect to duties. To teach his favorite subject at the underclass level, at the upperclass level, and at the graduate level and then direct research in that field is usually the best plan. When departments and divisions reach such a size that this can only be accomplished by a planned rotation of assignments, such rotations should be established. Details will vary but the general principles can usually be followed. Reasonable rotation of textbooks is equally desirable, if only to avoid stagnation. This is why only a very brave man will continuously use a textbook that he has himself written. The temptation to consider that the best way to present a topic has been found when one's own words have been embalmed in print is an extremely subtle one and should be resisted with all the means at one's disposal. The same might also be said of lecture notes. Age does not necessarily improve them.

Much has been written about the problems of recruiting and retaining teachers of chemistry. It is a problem that must be considered realistically and not in a vacuum. The supply of able and devoted young teachers seldom fills the demand. In part this is because of the great differences between starting salaries in the chemical industries and in our colleges and universities. These differences are very likely to persist. I would like very much to see starting salaries come much closer to starting industrial salaries. However, I hope they never become equal! The young person who plans to teach chemistry might well have his motives tested and his sincerity proved by financial tests. The profession of teaching, like that of the ministry, can always profit by some measure of devotion. There are so many ways open for a career of science that only those who can "gladly teach" should undertake academic careers.

A young person with a thorough training in his science, with an enthusiasm for subject matter, and with a keen interest in the problems and growth of human individuals will become a good teacher if he has a burning desire to do so. He will find the way to good teaching techniques. I do not decry the importance of teaching methods; they are very important! But they can never take the place of the other requirements noted. They can and will be acquired by the young teacher through either observation or reading. Courses in methods of teaching are to be highly recommended, provided they either outline the basic principle or describe established procedures. Practice teaching is also highly recommended. Undue attenuation is as objectionable in such classes as it would be in subject matter classes and leads to the same feelings of distaste.

The teacher must cultivate an open and inquiring

[1] Address presented on receiving the Scientific Apparatus Makers Award in Chemical Education, before the Division of Chemical Education at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March 30, 1954.

mind. He must avoid dogmatism both in his scholarship and in his teaching. He has a duty to present and to document dissenting views. Ample time should be devoted to the pros and cons of any scientific topic on which there is current difference of opinion. To neglect the controversial in current science is likely to result in a sterile course. Chemistry is a real, a growing science. Its experiments are never finished, its theories are never final, its controversies are never settled. The teacher must always present all sides of a controversial topic as fairly as he can and as time will permit. However, he has a further duty! *He must himself express an opinion. Neutralism* is as fatal to the development of independent thought as is *dogmatism*. Having done this he might well do his best to encourage disagreement on the part of his students. He is not engaged in winning an argument, he is attempting to foster independent thinking by his students. Weight of authority is one thing, *ex cathedra* statements are another!

The question of "how to teach" can never be answered. Kipling said, "There are four and twenty ways of writing tribal lays; and each of them is right." However, one can continuously re-examine his objectives, his tools, his methods, and his accomplishments. One can, as a matter of routine, rate intraterm and final examinations against a ranking of his class. One can review and re-evaluate textbooks and laboratory manuals. One can devise problem sheets and study aids. One can use for comparison the many standard tests now available. However, none of these is as important as is a critical and continuing self-examination.

The problem of the selection of subject matter is another instance where the decision must be that which fits best the ideas and procedures of the teacher. Our science has grown so rapidly that the traditions of the past regarding details of subject matter must be largely disregarded and new selections made. In many subject-matter fields of chemistry this is now under way. The most widely used texts in general chemistry today are those which have departed most widely from the traditions of Remsen and Alexander Smith. The same is true in elementary courses in organic chemistry.

THE GENERAL COURSE

My own teaching experience has been largely in the field of general chemistry, or to be more precise, in the field of the first courses given at the university level. Here is a fine field for the talents of a teacher. Here one has the rare privilege of helping to establish a foundation for the future.

The planning of courses in general chemistry demands an initial decision on the moot question as to whether the course is to be given as a professional or as a preprofessional course. It is my opinion that unless the group of students is one already committed to major study, the course should be planned as a preprofessional course. This need not mean that the subject matter or the method will be markedly different. However, it is important to make decisions with respect to emphasis and to standards of achievement. In a professional course one is entitled to set standards of competency, whereas in a preprofessional course one sets only standards of achievement and of understanding without regard to competency. It seems to me that among the objectives of the general course in chemistry should be the following general ones. First, to show the science of chemistry as an experimental science based upon experiment, although grounded on theory; "theory leads, experiment decides." It is equally important to show chemistry as a servant science. This is the old slogan popularized by Dr. Slosson. Chemist and nonchemist alike can gain both understanding and education by realizing that our science does not exist by itself or for itself. It exists as part of an intellectual whole which is greater than the sum of all of its parts. The first college course in chemistry should also contribute to an understanding of the scientific method. It has been said that science is a way of thinking. All of our students should be trained to realize the glories of scientific research and the place of research in our complex civilization. Related to this, of course, is the understanding that science is part of the culture of man. Too often, discussions of curricula and of the objectives of college training involve words and phrases designed to suggest to the unwary mind that knowledge comes in separated compartments and that an appreciation of human culture comes *only* from a study of what have lately come to be called "the humanities." All of us in university circles must share the blame for this warped point of view. Those of us who teach science have too often stressed unduly the contributions of 300 years of science and of the experimental method to the practical well-being of mankind. Since *we ourselves* have often overlooked the cultural significance and importance of science, it is not surprising that our colleagues in other scholarly disciplines have thought that the contributions of chemistry to general culture are either nonexistent or unimportant.

As a university student I had the pleasant good luck to have studied the history of philosophy with Professor Hartley Burr Alexander. I learned in his classes that philosophy is the keystone of all knowledge and that science contributes to a well-rounded view by man concerning all of his experiences, *physical*, *mental*, and *spiritual*. As teachers of chemistry we *can* and *must* do our share in contributing to the well-rounded development of our students as mature human beings in a noncompartmentalized world. If I may be permitted a scientific metaphor, we should combine synthesis with analysis from the point of view of the complete development of the human mind.

SERVICE COURSES

One who teaches courses in general chemistry has a heavy task and a marvelous opportunity when he is designated to teach "*service courses*" in chemistry. Sometimes a young teacher feels that his talents are being partly wasted when he is given such an assignment. This is not the case. Such an assignment constitutes a great challenge. It also constitutes a com-

pliment of the highest order. No departmental administrator assigns a young scientist to such courses unless he possesses great confidence in the ability of the teacher to rise to that challenge. When given such an assignment, one should examine the objectives of such a course as seen from the point of view of the students whose ultimate career objectives are in fields where chemistry is and always will be a *servant science*. We might well say to the class at least once a term, "this course is designed *not* to make you chemists or chemical engineers, *but* to contribute to your training *for* and your ultimate success *in* important areas of human knowledge and service." We might well repeat this to ourselves at least once a week! Our success with students in these areas will be measured not only by the interest and enthusiasm of our students and by their term credits and grades, but even more by their growing interest in the scientific aspects of their chosen careers. Where better than in chemistry can a young man develop interests and attitudes that will make him a medical scientist as well as a practicing physician? I have known general practitioners of medicine who are simultaneously practitioners of medical science. Such interest can be either fostered or retarded by the attitudes and ideas of teachers of science at all educational levels.

In nearly all of the divisions of what has come to be called "home economics" a continuing interest and enthusiasm for chemistry will be of great value to young women specializing in that field. Scientific agriculture has always been a field in which chemistry and chemical methods were tools for the investigator. The same is true of that magnificent borderline field of science known as biochemistry.

We must refer again to the importance of an understanding of science and the scientific method by all cultured citizens of a world that has been remade each ten years by science. There are objectives here beyond those ordinarily served by final examinations. What does it matter if the college alumnus tells you after 20 years, "the only thing I remember about chemistry is the formula for water"? The chances are good that he remembers very much more than that, and that the philosophical understanding gained in your class will stay with him. It has become so much a part of his thinking that he no longer relates it to your class. This is real success! This is the real goal for the devoted teacher. What has been said about "service courses" in general chemistry applies with equal force to more advanced courses taught to students in curricula other than chemistry.

FACULTY RELATIONS

It may be that undue emphasis has been placed so far upon teaching as an individual enterprise. Teaching starts there, but it does not stop there. In most universities, teaching is a group enterprise. It demands organization, a great deal of organization! It demands administration, a great deal of administration! Since these things are true, it is not surprising that one sometimes finds *too much* organization and *too much* administration. This is equally true regarding the much discussed point of faculty participation in administration. It is my considered opinion that *more emphasis* should be placed upon a thorough and complete understanding of objectives and procedures in education and *much less emphasis* upon formal details of organization. A faculty in any field and in all fields should exist as a community of scholars and teachers. Free, frequent, and oftentimes informal discussions are much better than the highly formalized schemes of administration so often relied upon to insure "faculty democracy." Much more faculty democracy can be induced at the luncheon table or over martinis than can ever result from formal committee meetings with five to four votes. Minor details of procedure should never be brought to a departmental staff or a faculty. General policies should grow out of thorough and complete understanding and should involve near unanimity of opinion based upon complete (often long-winded) discussion. It follows from this that a departmental administrator must at times have the courage of his convictions but that he should never attempt to impose dogmatic opinions upon the staff of a department. He should, however, protect members of the staff from the very forceful colleague who attempts to push through changes in policies that have not been carefully thought out.

A college faculty has the responsibility for maintaining an atmosphere of enthusiasm about learning, an atmosphere in which youthful genius can flourish. This is only accomplished where one finds much more vigor than he does inertia. It is a place where complacent satisfaction has been driven out by constructive dissatisfaction. Alfred North Whitehead has said, "In the history of education, the most striking phenomenon is that schools of learning, which at one epoch are alive with a ferment of genius, in a succeeding generation exhibit merely pedantry and routine. The reason is that they are overladen with inert ideas."

In setting up and evaluating needs for the development of a vigorous intellectual atmosphere we must always place men first. Thereafter, in any scientific field comes the library and the laboratory. In the laboratory one needs, first of all, equipment; finally, one needs buildings. I have seen good teaching and the development of outstanding scientific enthusiasm in laboratories where the desks were planks laid on sawhorses, but there were *men* in those laboratories. I have seen magnificent research carried on with meager equipment and in antiquated buildings, but there were *men* in those buildings. Thus, I close as I began, with emphasis on the teacher.

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SOME FUNDAMENTALS OF DESIGNING TABLES OF DATA[1]

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IN EXCHANGING shop talk with other report editors, I am always amused at the wide variety of tasks management sees fit to assign to the report editor; the job seems to be the catch-all for any unassigned duties. Yet I am sure that teaching has not been recognized as one of the basic duties of good technical editing. A writer should be able to learn something from the editing of his report, so that his next report will be better. If a writer's sixth report requires the same kind and amount of editing as his first, something is radically wrong. The blame probably can be placed upon unreasonable editorial requirements or upon poor author-editor relations.

Since poor spelling and grammar are the most common and most obvious weaknesses of technical writers, I suppose each of us has his own subtle methods of teaching these subjects to his writers.

But what do you do about teaching your men to report data intelligently? Since space is limited, I shall discuss only one phase of the problem, the design of tables of data. I am sure that on the problems of spelling and grammar all of us have been tempted to give up and just correct the mistakes without trying to improve our writers. But we cannot do that with tables of data because the scientist who collects the data is best equipped to interpret and evaluate them, and the design of a good table is dependent upon interpretation and evaluation.

So I have assembled a few fundamentals of tabulation which I have found useful in helping others design tables for the presentation of their data. These fundamentals can best be explained by examples, so I have "faked" some tables to illustrate my points. To borrow a technique from advertising, we might label almost all the A tables "Before" and the B ones, "After."

(1) *If four or more items of data are given, they should be presented in tabular form.*

In Example 1 notice how much easier it is to understand the table.

(2) *Every table should have both a number and a title.*

The title should be brief, but it should clearly identify the information contained, with reference to the text. If you follow the practice of listing table titles in the Table of Contents, your authors will realize that they cannot have a long list of identical titles but must individualize each.

(3) *Even qualitative comparisons and contrasts are more easily understood in table form.*

In Example 2, as in Example 1, reporting the data in a table is an aid to understanding.

Incidentally, it is important that your writers realize that not all data are numerical.

(4) *Columns and rows must have identifying headings.*

(5) *Units of measurement must be given.*

Usually, the column or row headings are the logical locations for units. Lack of such identification seems to be the most common failing of tables.

(6) *The same unit of measurement should be used for comparable properties or dimensions.*

EXAMPLE 1

The daily low-X diet, called Diet A, was prepared by adding to 10 g. of skim milk the equivalents of 0.0003 g. of iron from $FeSO_4 \cdot 7H_2O$, 0.0001 g. of zinc from $Zn(C_2H_3O_2)_2$, 0.0001 g. of copper from $CuSO_4 \cdot 5H_2O$, 0.0026 mg. of iodine from KI, and 0.0008 g. of manganese from $MnSO_4 \cdot H_2O$.

TABLE 1
Low-X Control Diet, Diet A

Mineral	*Mg./10 g. skim milk*	*Source*
Fe	0.3	$FeSO_4 \cdot 7H_2O$
Zn	0.1	$Zn(C_2H_3O_2)_2$
Cu	0.1	$CuSO_4 \cdot 5H_2O$
I	0.0026	KI
Mn	0.8	$MnSO_4 \cdot H_2O$

EXAMPLE 2

Streaked animals, ss, can be produced only by the following matings: (*a*) streaked ss × streaked ss, (*b*) heterozygous Ss × streaked ss, (*c*) heterozygous Ss × heterozygous Ss. In mating (*a*) all offspring will be streaked; in mating (*b*) in which one of the parents was streaked ss and the other heterozygous Ss, half of the offspring will be streaked; in mating (*c*) in which both parents are heterozygous, one-fourth of the offspring will be streaked.

TABLE 2
Matings Required to Produce Streaked Animals, ss

Parents	*Streaked offspring, ss*
Streaked ss × streaked ss	All
Heterozygous Ss × streaked ss	1/2
Heterozygous Ss × heterozygous Ss	1/4

[1] Presented at a round table discussion on Problems of Technical Editing sponsored by the American Documentation Institute, Washington, D. C., Nov. 6, 1953.

EXAMPLE 3

TABLE 3A

Test	*Sample*	*Duration, min.*	*Ash type*	*Velocity, f. p. s.*	*Concn., gr./ft.³*	*Ash impinged, g.*	*Ash collected, g.*	*Count rate, c. p. m.*	*Steel collected, g.*	*Steel expected, g.*
1	2	10	..	1050	..	..	..	33	...	...
2	2	10	..	1050	..	..	..	76	...	...
3	1	10	A	1050	1.3	1.0	0.71	2523	0.024	0.04
4	1	10	A	1050	1.3	1.0	0.54	1446	0.014	0.04
5	1	10	A	1050	1.3	1.0	0.58	1479	0.014	0.04
6	2	10	A	1050	1.3	1.0	0.54	2227	0.021	0.04
7	2	10	A	1050	1.3	1.0	0.53	2261	0.021	0.04
8	2	10	B	1050	1.3	1.0	0.23	473	0.004	0.015
9	2	10	B	1050	1.3	1.0	0.17	423	0.004	0.015
10	2	10	B	1050	1.3	1.0	0.16	502	0.005	0.015
11	2	10	B	800	1.6	1.0	0.23	395	0.004	...
12	2	10	B	800	1.6	1.0	0.26	331	0.003	...
13	2	10	B	800	1.6	1.0	0.28	376	0.003	...
14	2	10	A	800	1.6	1.0	0.92	700	0.006	...
15	2	10	A	800	1.6	1.0	1.00	629	0.006	...

Note: fly ash type A, untreated; fly ash type B, Aerotec separated. Sample 1, flat surface; 2, curved surface.

Notice in Table 1 of Example 1 that all the weights are converted to milligrams.

(7) *The units of measurement used in a table should all be of the same system, such as metric, English, or apothecary.*

Of course, your engineers will insist that their convention demands a mixture. You may need to ask them to cite examples from printed literature to justify their usage.

(8) *If an item is repeated several times in a table, probably it should appear just once in the title, in a footnote, or in a column or row head.*

Often such repetition obscures important similarities, as you can see by inspection of the two tables in Example 3.

The third and seventh columns of Table 3A have been eliminated in Table 3B by inserting the information in the title. The fourth, fifth, and eleventh columns of Table 3A have been eliminated in Table 3B, and the use of the information in inserts serves to group related data.

See Example 4, also.

(9) *Column and row headings should be used to group related data.*

See the B tables of Examples 3 and 4.

TABLE 3B

Erosion Data for 10-Minute Impingement of 1-g. High-speed Fly Ash on a Radioactive Steel Alloy

Steel surface[a]	*Test*	*Ash recovered, g.*	*Counting rate, c./min.*	*Collected, g.*
2	1	..	33	...
	2	..	76	...
	1.3 gr./ft.³, ash A[b] *at 1050 ft./sec.*			[c]
1	3	0.71	2253	0.024
	4	0.54	1446	0.014
	5	0.58	1479	0.014
2	6	0.54	2227	0.021
	7	0.53	2261	0.021
	1.3 gr./ft.³, ash B[b] *at 1050 ft./sec.*			[d]
2	8	0.23	473	0.004
	9	0.17	423	0.004
	10	0.16	502	0.005
	1.6 gr./ft.³, ash B[b] *at 800 ft./sec.*			
2	11	0.23	395	0.004
	12	0.26	331	0.003
	13	0.28	376	0.003
	1.6 gr./ft.³, ash A[b] *at 800 ft./sec.*			
2	14	0.92	700	0.006
	15	1.00	629	0.006

[a] 1, flat; 2, curved.
[b] A, untreated; B, Aerotec separated.
[c] 0.04 g. expected.
[d] 0.015 g. expected.

EXAMPLE 4

TABLE 4A

Summary of Ozonolysis Runs

Ozonolysis run no.	*Ozone concentration, carrier gas, solvent, and temperature*	*Critical variables in processing*	*Yield, %*
69	10% O_3/N_2 in 2.83 g. X, 32 ml. HAc, 20–25°C.	Heated 2 hr. at 90–95°C.; half charge (5%) O_3 passed through at 25°C. over 15-min. period.	Charred
70	5% O_3/N_2 in 0.85 g. X, CCl_4/HAc: 31/8 ml., 23–24°C.	Allowed to stand 3 days at 25°C.; added 15 ml. HAc; refluxed 0.5 hr.	80
71	10% O_3/N_2 in 2.83 g. X, 32 ml. CCl_4, 21–24°C.	Added 30 ml. HAc; heated 2 hr. at 80–95°C.; 1 ml. H_2O added; half charge O_3 added during 30 min. at 25°C.	40
72	5% O_3/N_2 in 0.85 g. X, CCl_4/HAc: 31/8 ml., 23–24°C.	Held 2 hr. at 25°C.; added 15 ml. HAc; refluxed 0.5 hr.	77

TABLE 4B
Summary of Ozonolysis Runs 69 to 72

Run no.	Ozonization: O_3/N_2, %	X, g.	Solvent, ml.	Temp., °C.	Decomposition: O_3/N_2, %	Treatment	Time, hr.	Temp., °C.	Yield, %[a]
69	10	2.83	HAc 32	20–25	5	Heated	2	90–95	Charred
						O_3 added	1/4	25	
70	5	0.85	CCl_4 31	23–24		Held	72	25	80
			HAc 8			15 ml. HAc added			
						Refluxed	1/2		
71	10	2.83	CCl_4 32	21–24	5	30 ml. HAc added			40
						Heated	2	80–95	
						1 ml. H_2O added			
						O_3 added	1/2	25	
72	5	0.85	CCl_4 31	23–24		Held	2	25	77
			HAc 8			15 ml. HAc added			
						Refluxed	1/2		

[a] Based on amount of X used.

EXAMPLE 5

Table 5A
Some Physical Constants of the Brominated Hydrocarbons Used

Chemical	CBr_4	$C_2H_4Br_2$	CH_2Br_2	C_2Br_4
Specific gravity	3.42	2.055	2.495	..
Boiling point, °C.	189.5	108	98.5	226

TABLE 5B
Some Physical Constants of the Chlorinated Hydrocarbons Used

Chemical	Specific gravity	Boiling point, °C.
CCl_4	1.59	−22.6
$CHCl_3$	1.50	62.0
C_2HCl_3	1.465	87.2
C_2Cl_4	1.63	120.8

EXAMPLE 6

TABLE 6A
Effect of Filter in Gas Line

Time	Meter readings, ft.³	Flow rate, c. f. m.	Temp., °F.	ΔP across trap, in. Hg
10:00	66,830	..	74	5.2
10:30	67,792	31	70	5.2
11:00	69,001	40	71	5.3
11:30	70,210	31	72	5.7
12:00	71,172	40	72	6.2
12:30	72,381	31	73	6.8

TABLE 6B
Effect of Filter in Gas Line

30-min. intervals	Flow rate, ft.³/min.	Temp., °F.	ΔP across trap, in. Hg
1	..	74	5.2
2	31	70	5.2
3	40	71	5.3
4	31	72	5.7
5	40	72	6.2
6	31	73	6.8

EXAMPLE 7

Diet B included Diet A plus 20 micrograms of X (from XCO_3) per 10 g. of skim milk. Diet C was Diet A enriched with 20 micrograms of X (from X_2O_3) per 10 g. of skim milk.

TABLE 7A
Results of Feeding Rats Low-X Diet A[a] for 8 Weeks

Rat	Weight, g. Starting	Weight, g. Final	Gain
A_1	70	135	55
A_2	100	168	68
A_3	80	186	106
A_4	100	165	65
A_5	130	202	72
A_6	75	117	42
A_7	110	150	40
A_8	80	152	72
A_9	85	135	50
A_{10}	90	148	58
Average			63.8

[a] See Table 1.

TABLE 7B
Comparison of Rat Weight Gains on Three X Test Diets[a] for 8 Weeks

Diet	X added to diet A[b]: g./10 g. milk	Source	Average gain, mg.
A[b]	..	..	63.8
B	20	XCO_3	75.15
C	20	X_2O_3	75.3

[a] Each diet was fed to a different group of 10 rats.
[b] See Table 1.

(10) *Similiar tables should be set up in the same manner within a given report.*

If the data of both tables in Example 5 are to appear in the same report, they should be set up in the same manner, preferably like Table 5B.

(11) *Whenever possible, a table should be set up so that it can be typed on the page in the normal manner.*

See Example 3.

(12) *For ease of comparison, a table should be set up so that all the data in a given column have the same unit. If the items in a column have different units, each item should be centered in the column instead of aligned in the usual manner by digits or the decimal point.*

See Example 5.

(13) *Data of only record interest should not be included in a report table.*

The clock times listed in Table 6A of Example 6 are not pertinent to the problem. In fact, listing them obscures the pertinent fact that the readings were made at 30-min. intervals.

(14) *Often a summary table should be presented in the report and the supporting or record tables may be placed in an appendix.*

In Example 7, Table 7B is a summary of the paragraph, of Table 7A, and of two similar tables giving the results of feeding diets B and C. Table 7A and the other two tables may be placed in an appendix to the report. Of course, such decisions are dependent upon the purpose of the report.

A MICRO GAS GENERATOR

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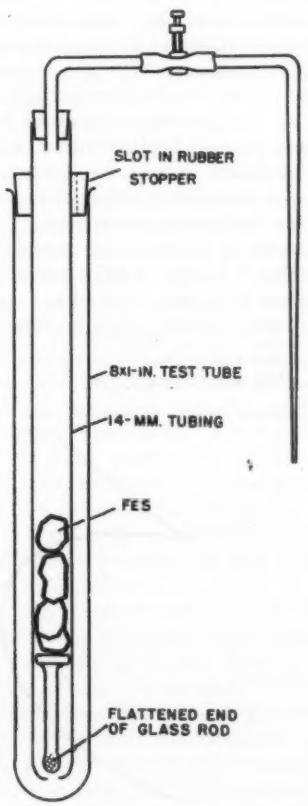
THE illustration shows a micro Kipp generator for H_2S which we have found more satisfactory than any previously described. Several particular features must be observed.

Precautions. Surface tension effects can be very pronounced in a micro apparatus and destroy the effectiveness of the hydrostatic head in producing gas pressure. The following must not be *less* than specified: (1) the clearance between the inner test tube wall and the outer wall of the gas tube (4 mm.); (2) the diameter of the hole in the bottom of the gas tube (3–4 mm.); (3) the clearance between the glass "nail head" and the inner wall of the gas tube (1.5–2 mm.). The use of glass wool in place of the glass rod makes for unsatisfactory capillary effects. The use of more than three or four chunks of FeS (each about 4 mm. in diameter) makes for unsatisfactory performance.

Operation. The amount of HCl (6 *M*) should be such that its level is approximately 1 in. below the larger rubber stopper when the inner tube is empty. For convenience in recharging, a mark should be made on the test tube designating the level to which this amount of HCl fills the test tube when the inner tube is removed. At the end of each laboratory period the center tube is removed, rinsed inside and out under a tap, and stored separately. If any tiny pieces of FeS have crumbled away, they are all found in the bottom of the test tube. The students separate these by decanting the HCl into another container for storage.

This generator was made by each student and used in a course where over 100 students used the laboratory daily. H_2S fumes and generator operation completely ceased to be problems. With slight modifications the generator can be used for CO_2 and other gases.



BAKHUIS ROOZEBOOM AND THE PHASE RULE[1]

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From the results obtained in the more simple systems we may confidently expect that we shall in due time also understand the reciprocal action of substances in more complicated systems and that from the present rock fragments an harmonic structure will arise that will stand out as a revelation of the exalted thoughts of the Creator.

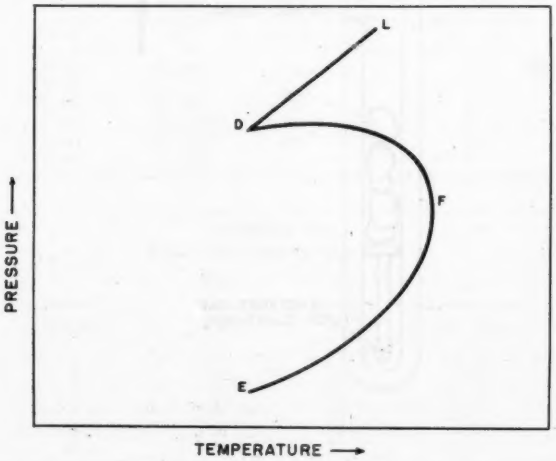
—Bakhuis Roozeboom

THIS year commemorates the centenary of the birth of Hendrik Willem Bakhuis Roozeboom, the foremost exponent of Gibbs' phase rule. Born on October 24, 1854, in Alkmaar (Holland), the only child of Jan Hendrik Bakhuis Roozeboom, a bookkeeper, and Maria Rensen, the future chemist received his early training in theoretical and experimental chemistry from the principal of the local high school, Dr. J. D. Boeke. He graduated at the head of all the graduates in the three high schools in the province of North Holland (at Amsterdam, Haarlem, and Alkmaar). While studying Latin and Greek in the next two years in preparation for his admittance to the university of his choice, he continued his chemical studies in Boeke's laboratory. At the recommendation of Boeke, J. M. van Bemmelen, Boeke's brother-in-law, who was principal of a secondary school at Arnhem, employed Roozeboom as a temporary assistant in some work on soil analysis for the Dutch government. Van Bemmelen's appointment as professor of inorganic chemistry at the University of Leiden in 1874 induced Roozeboom to matriculate as a student in Leiden. Lack of funds soon forced him to accept outside employment in a private testing laboratory, owned and operated by Dr. J. Th. Mouton in The Hague.

When the laboratory burned down in 1878 Roozeboom, at the suggestion of Mouton, returned to Leiden and was fortunate in obtaining an appointment as lecture assistant to van Bemmelen, which enabled him to continue his studies. Through the help of his employer, who fully recognized the potentialities of his pupil and had disregarded the custom of hiring a graduate assistant, Roozeboom was excused from attending lectures. Spending his days in the laboratory and devoting evenings to theoretical studies, he was able to obtain his degree of *candidatus matheseos, astronomiae, physices et chemices* in February, 1881. The next year, in April, 1882, he passed his final doctoral examination and on June 7, 1884, he was awarded the Ph.D. degree with a thesis on "The hydrates of sulfurous acid, chlorine, bromine, and hydrochloric acid." His marriage to Miss C. E. Wins in 1879 led him to accept a part-time job at a girls' high school in Leiden, which to him was more of a chore than a pleasure. His assistantship was changed to a more remunerative lecturership in 1892 and four years later he became van't Hoff's successor as professor of inorganic chemistry at Amsterdam. Here he remained until his death from pneumonia on February 7, 1907.

In his scientific career we can recognize three distinct periods: first, from 1881 to 1887; second, from 1888 to 1895; and third, from 1896 to 1907. In his formative first period Roozeboom was strongly attracted to the work of Deville and his co-workers. His doctoral thesis, written in French and published in the *Recueil*, contains at the end ten statements, one of which reads as follows: "In 1857 Deville founded the dissociation theory." As a matter of record Roozeboom's first publication (in 1881) dealt with the dissociation of tertiary butyl bromide. This was followed by a systematic study of gas hydrates, a field in which Deville's pupil Debray and other French chemists had been active. Roozeboom's data were published in the *Recueil* and communicated by van Bemmelen in several meetings of the Royal Academy of Sciences in Amsterdam in 1884 and 1885. Roozeboom was able to give a graphical representation, on a pressure-

[1] Presented at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.



temperature diagram, of the possible equilibria between two mutually soluble substances, capable of forming solid compounds and appearing in three states of aggregation (the term "phase" was still unknown). This was the first ray of light in the chaos of conflicting data that had appeared in the chemical literature between 1864 and 1884. Roozeboom's data, particularly those on hydrobromic acid and water, attracted the attention of van der Waals, professor of theoretical physics at Amsterdam, who was acquainted with the work of his colleague Willard Gibbs of Yale University. Having studied the thermodynamics of monovariant three-phase systems, van der Waals was able to interpret Roozeboom's pressure-temperature curve *EFD* (see the figure) and also the unexpected part *DL*. Applying the Clapeyron equation to the 3-phase equilibrium solid hydrate-solution-vapor, van der Waals derived the expression:

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{(W_{\text{hydrate}} - W_{\text{solution}})\Delta H_{\text{vapor}} + \Delta H_{\text{fusion}} + \Delta H_{\text{dilution}}}{T((W_{\text{hydrate}} - W_{\text{solution}})V_{\text{vapor}} + V_{\text{solid}} - V_{\text{solution}})}$$

where $W_{\text{hyd.ate}}$ and W_{solution} are the number of moles of water associated with one mole of HBr in the hydrate and with one mole of HBr in solution,

ΔH_{vapor} is the heat of vaporization of one mole of water vapor,

ΔH_{fusion} is the heat of fusion of one mole of hydrate in its own water,

$\Delta H_{\text{dilution}}$ is the heat of dilution of hydrate water to solution water,

V_{vapor} is the volume of one mole of water vapor,

V_{solid} is the volume of one mole of solid hydrate and

V_{solution} is its volume in solution.

If one neglects $\Delta H_{\text{dilution}}$ and the last two terms in the denominator, all of which are very small, it is seen that the curve must have a vertical tangent at *F* for $W_{\text{hydrate}} = W_{\text{solution}}$ and a horizontal tangent near *D* when

$$W_{\text{hydrate}} - W_{\text{solution}} = -\frac{\Delta H_{\text{fusion}}}{\Delta H_{\text{vapor}}}$$

When this conclusion had been reached, a conference was held early in 1886 in Leiden, attended by van Bemmelen, Roozeboom, Lorentz, Kamerlingh Onnes, and van der Waals, in which the last-named gave a detailed account of Gibbs' phase rule and expressed his opinion that the point *D* in the diagram must be a quadruple point and *DL* part of a new three-phase curve. This lecture and the prospects it opened for further research were a revelation to Roozeboom, who plunged at once into a study of Gibbs' celebrated article "On the equilibrium of heterogeneous substances," which although already eight years old had been completely ignored by chemists as being "algebra and incomprehensible" and hence never systematically applied by anybody.

Not content with Gibbs' publication, Roozeboom also went through a student note book covering van der Waals' lectures on thermodynamics. With the help of Kamerlingh Onnes he thereupon devised an arrangement which permitted him to open and close a glass stopcock at pressures up to 10 atm. and to analyze the solid phase in equilibrium with the solution and vapor along the curve *DL*. This happened to be a new, hitherto unknown hydrate, $HBr\text{-}H_2O$. The quadruple point *D* was found to lie at $-15.5°$ and 2.5 atm. and was the first example of its kind. The conditions under which the four possible three-phase curves branching out from a quadruple point can be obtained were realized by Roozeboom, not only for the gas hydrates previously examined but also for the system $NH_4Br\text{-}NH_3$, in which the volatile constituent is not water but ammonia. This epoch-making work, carried out by Roozeboom alone in the years 1882–86, established his reputation as a first-class scientist. Van Bemmelen, always eager to further the interests of his able assistant, succeeded, after two abortive attempts in 1888 and 1889, in having Roozeboom elected as a member of the Royal Academy in 1890. At the request of Ostwald, Roozeboom published his work, until then only available in French, also in the newly founded *Zeitschrift für physikalische Chemie*, and in this way Roozeboom became more widely known outside his home land.

In his second period, that of active exploration of the new field of research, from 1888 to 1895, Roozeboom, as newly appointed lecturer in chemistry, soon enjoyed the help of some talented co-workers. His very first pupil was Stortenbeker, with whom he studied the system chlorine-iodine. The second was Schreinemakers, who assisted in clarifying the systems $CaCl_2\text{-}H_2O$ and $Fe_2Cl_6\text{-}H_2O$, in both of which the existence of several unknown hydrates was established.

Ternary systems, for which Roozeboom introduced his well known triangular diagram, were also studied, again with the aid of Schreinemakers. One of the first of these was the system $Na_2SO_4\text{-}MgSO_4\text{-}H_2O$, in which a double salt (astrakanite) occurs. This was followed by a detailed study of the systems $PbI_2\text{-}KI\text{-}H_2O$ and $Fe_2Cl_6\text{-}HCl\text{-}H_2O$, in which ternary compounds and quintuple points were located.

In his final, most productive period of activity, from 1896 to 1907, as professor of inorganic chemistry and head of the laboratory built by his predecessor, Roozeboom was no longer in a position to do research and confined himself to directing and stimulating the researches of his students. Contrary to all expectations, the change in environment from the peaceful, small, provincial city of Leiden to the bustling metropolis of Amsterdam did not in the least disturb Roozeboom. As one of his friends said: "If one did not know that Roozeboom had lived in Leiden, one might well take him for a born Amsterdamer." The daily contact with a large number of assistants: Cohen, Smits, Jaeger, van Laar, and others acted as a stimulant on Roozeboom. His teaching load was heavy: in addition to the freshman course in general chemistry, supplemented by an additional course for chemistry

students, he gave a course in his favorite subject, The Phase Rule and Its Applications, for students working for their Ph.D. degree. Although he preferred research to teaching, he proved to be a first-class teacher by his zest, his originality, and his eloquence. He was always in excellent humor and a trusted adviser and friend to his students.

When his compatriot J. W. Retgers (1856–96), a mining engineer with a Ph.D. degree from the University of Leipzig (1889), in a series of 12 articles on "isomorphism" published in the *Zeitschrift für physikalische Chemie*, had called the attention of physical chemists to the large group of so-called mixed crystals, Roozeboom decided to consider these from the standpoint of the phase rule. In 1899 he published his brilliant and much-quoted article on "Erstarrungspunkte der Mischkristalle zweier Stoffe" (the freezing points of solid solutions of two substances). It should be noted that the term mixed crystal is seldom if ever used nowadays, and the term solid solution, first proposed by van't Hoff in 1890, is now generally accepted, at least in English-speaking countries.

Using van Rijn van Alkemade's graphical method of plotting the ζ-function (free energy) against the concentration, Roozeboom predicted the existence of five types of solid solutions formed by binary systems. These five types have subsequently been found experimentally by his pupils and by others and are discussed in all modern texts on physical chemistry.

The following year (1900) Roozeboom published a critical examination of the iron-carbon system, based on the experimental data of Roberts-Austen in England and the researches of Le Chatelier in France. The diagram was completed by Roozeboom by the addition of what has since been called the *solidus* line which separates a heterogeneous region of liquid + solid solution from a solid solution area. The changes in the diagram necessitated by the existence of a δ-modification of iron were also discussed and a possible solution of carbon in α-iron was, likewise, taken in account. This study attracted widespread attention outside Holland and led to intensive researches dealing with this highly important system on both sides of the Atlantic.

As a fitting climax to two decades of phase-rule studies, Roozeboom undertook the publication of a comprehensive text on this topic. A brief introductory text of 72 pages had already been published by Meyerhoffer in 1893 shortly after Ostwald had translated Gibbs' thermodynamic studies into German (in 1892). It was said at the time that Gibbs was "too busy" to write a preface to Ostwald's translation, and the latter in his autobiography pointed out that for more than a decade the English and the Americans had to read Gibbs' work in German, until finally Yale University, after Gibbs' death in 1903, got around to publishing a new edition.

Bancroft, who had studied in Amsterdam under van't Hoff in 1893, published in 1897 a volume of 255 pages entitled "The Phase Rule," in which he says:

> I have tried to present the subject of qualitative equilibrium from the point of view of the Phase Rule. That such a treatment should be possible is due largely to the work of H. W. Bakhuis Roozeboom, who has done more than any one else to show the importance and significance of Gibbs' Phase Rule.

This text, containing many inaccurate and unreliable data, failed to distinguish between the essential and the nonessential and was soon forgotten. The terms non-variant, mono-variant, di-variant, etc., introduced by Bancroft have, however, been taken over by Roozeboom and later writers on the subject.

The first volume of Roozeboom's monumental work, "The Heterogeneous Equilibria from the Standpoint of the Phase Rule," appeared in 1901. This volume dealt with systems of one component while the first part of Volume II discussed binary systems. When it came out in 1904 Ostwald (*1*) stated that it was one of the few books that required no explanation for its appearance, it being an indispensable part of every physicochemical library. Four years laters later Volume II was supplemented by two additions written by Roozeboom's pupils A. H. W. Aten and E. H. Büchner. Volume III, published in 1911, was written by Roozeboom's pupil Schreinemakers, who had become van Bemmelen's successor in 1900.

Roozeboom's untimely death at the age of 52 deprived him of the recognition and honors which would have been given him for his incomparable achievements. Deeply religious and sharing the aversion of common people to speculative philosophy, he looked upon the phase rule as an expression of divine intent to regulate the material world. He was free from personal vanity and devoid of any trace of publicity-seeking spirit. The only signal recognition of his merits was his election to the Royal Academy of Sciences. On the foundations laid by his pioneering efforts, numerous laboratories in Holland and elsewhere have expanded our knowledge of chemistry. The study of the origin of minerals and rocks, initiated by the phase rule, found its fulfillment in the establishment in 1906 of the Geophysical Laboratory in Washington, an event which was greeted by Roozeboom with particular satisfaction. The phase rule work begun by Roozeboom, first in Leiden and later in Amsterdam, was continued by his pupils: in Amsterdam by Smits, in Leiden by Schreinemakers, in Utrecht by Cohen and Kruyt, in Groningen by Jaeger, and in Delft by Reinders and Scheffer. From funds contributed by friends and former students of Roozeboom the Royal Academy of Sciences has, from time to time, awarded a Bakhuis Roozeboom medal, to honor the memory of one of its most distinguished members. The first recipient of this award was F. A. H. Schreinemakers (1916). Later medalists were G. Tammann (1923), J. J. van Laar (1929), P. W. Bridgman (1933), A. L. Day (1939), and W. Hume Rothery (1950). Roozeboom's contemporaries welcomed his phase-rule studies with varying degrees of appreciation. Many of his followers, "more royalist than the king," were guilty of unjustified exaggerations. Others, like Ostwald and Ban-

croft, appraised Roozeboom's work at its true value. Nernst, however, claimed that chemistry would be practically degraded to a triviality if one were guided only by Roozeboom's emphasis on the phase rule (*2*). Even van't Hoff, in lecturing on the phase rule (*3*), merely stressed its pedagogical value in the treatment and the classification of various systems in equilibrium. Cohen, who was on friendly terms with both van't Hoff and Roozeboom, admits (*4*) that a genius like van't Hoff who, in his "Études de dynamique chimique" had introduced the principle of the incompatibility of condensed systems, could get along without knowing anything about the phase rule. On the other hand, for less gifted individuals the phase rule retains its great heuristic value. Van't Hoff, as is well known, dealt mainly with homogeneous systems, involving the mass law, in which case equilibria are described by means of an equation. In heterogeneous systems this equation is replaced by a geometrical representation of the conditions of equilibrium. Bancroft, in comparing the phase rule and the mass law, has this to say: (*5*)

> There seems to be a feeling that the phase rule and the mass law are antagonistic in some mysterious way; whereas the phase rule gives the broad, general, qualitative classification, while the mass law supplements this by giving quantitative relations in and between the phases. If one knows where the railroad tracks are (phase rule), one can predict with absolute accuracy where the trains will run and in the case of a single-track road, one can point out the only places where trains going in the opposite direction can pass; but one cannot, unless one is a Sherlock Holmes, tell the number of trains per day or the speed at which they travel. If one has the latest time table (mass law), one knows a lot of quantitative data, such as the time of arrival and departure of trains, the equipment etc. One can also deduce the mean speed (reaction velocity), the length of the run made by the dining car, etc. If the locomotive cannot make steam owing to cold weather and therefore behaves like an imperfect gas, the time table does not hold. The time table, like the mass law, holds accurately only under favorable conditions. Nobody ever discusses the relative merits of tracks and time tables and it is not clear why the kindred problems of phase rule and mass law should have such a fatal fascination for some people.

In considering the relative standing of van't Hoff and Roozeboom, Bancroft (*6*) distinguishes three groups of scientific men, in the first of which he places those who discover fundamental relations. Gibbs and van't Hoff belong to this very small group. In the second group, to which Ostwald and Roozeboom belong, are the men who do not make the great discovery but who see the bearing of it and hence "preach the gospel to the heathens." The third group contains "the rest of us."

In these days of turmoil and strife where men of good will in different countries are separated by what Churchill has called "iron curtains" and thus prevented from friendly intercourse with their fellow men, it may not be amiss to conclude this brief review of Roozeboom's life work with a quotation from Duhem's "Thermodynamics and Chemistry" (*7*), which, as the author informs us, was written as a tribute to the genius of J. W. Gibbs, an American Lavoisier and the initiator of another "chemical revolution." Duhem, in the preface to his book, says:

> At the start the whole algebraic doctrine of Gibbs did not find in the country of its creator experimentalists to transform it into chemical theory; it found them in Holland. From this again, we may learn a lesson. The full discovery of the truth requires the concurrence of all peoples, their diverse intellectual aptitudes, their different ways of conceiving an idea, of developing it and of expressing it. In this respect exclusiveness would again be punished by sterility.

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SPRING COURSE IN CHEMISTRY OF THE FATS AND OILS

A NOVEL graduate-school course will be offered to chemists in the New York area at the Polytechnic Institute of Brooklyn in the spring of 1955, in the evenings, a special topics course entitled Chemistry of the Fats and Oils. It is a one-semester series of 15 two-hour lectures on Wednesday evenings. The course has special appeal to chemists in the various fats and oils industries and may be taken on a degree or nondegree basis.

The subject matter will include latest theory, reaction mechanisms, and new developments in the field. The occurrence, distribution, structure, isolation, purification, and analysis of animal and vegetable fats and oils will be covered. Hydrolysis, saponification, hydrogenation, oxidation, autoxidation, ozonization, and polymerization of fats and oils and the preparation and properties of fatty acids and their derivatives will receive special emphasis. Drying oils, alkyd resins, and chemical utilization of waste fats will be treated in some detail. Dr. Norman O. V. Sonntag of the Research and Development Department of Colgate-Palmolive Co., Jersey City, New Jersey, will be in charge of the course.

Further information regarding registration and qualifications may be obtained either from Dr. Sonntag or from Professor R. E. Kirk, Dean of the Graduate School, Polytechnic Institute of Brooklyn, 99 Livingston Street, Brooklyn 1, New York.

THE LANTHANIDE CONTRACTION

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THE consequences of the change in size in the lanthanide series are well known and the discussions of the effects of the lanthanide contraction in most reference sources are quite adequate. However, the discussions of the nature and magnitude of the lanthanide contraction itself and its relationship to size changes in the periodic table as a whole are usually misleading to the student. The contraction is commonly explained simply as the result of increased nuclear charge[1] or as the result of increased nuclear charge without compensation for it through alteration of the outer arrangement of electrons.[2] While such statements are not in error, the first does not indicate the magnitude of the contraction and the second misleads the student through the implication that the contraction would be smaller if the outer arrangement of electrons were altered. The contraction in the lanthanide series is smaller than that encountered in any extended group of elements in any period of the periodic table, with the exception of the actinide series, where the contraction would be expected to be comparable.

Graduate students in my own classes have been asked to study the information available and then write a discussion of the lanthanide contraction in their own words. This has usually resulted in statements which were not merely misleading, but erroneous.

With only two exceptions the sizes of atoms[3] increase with increasing atomic number within a family, since a new shell is added for each succeeding period. In a given period the size of the atoms generally decreases with increasing nuclear charge, since no new shells are introduced. The inert gas atoms appear to be striking exceptions to the general shrinkage within a period. The atomic radius of each of the inert gases is considerably larger than that of the preceding halogen. The increase in size is sometimes attributed to the mutual repulsion of electrons in a closed shell, but the atomic radii of the inert gases are really nonbonded van der Waals radii. If compared to the van der Waals radii for the other nonmetals there is a regular decrease through the period including the inert gases. There are a few other instances of small increases in size through a period. Most of these occur for metals at the ends of the transition series or just following the transition series and can probably be attributed to differences in structure and in the number of valence electrons available for bonding. There is an appreciable increase in the atomic radii of europium and ytterbium in comparison to the preceding elements while no increase is observed for the corresponding trivalent ions. The size increase in the case of the free metals is attributed to the presence of dipositive ions giving only two valence electrons for metallic bonding instead of the three usually encountered for lanthanide metals. The structures of these two metals also differ from the hexagonal, closely packed structure encountered for most of the lanthanide metals.[4] Europium and ytterbium might be expected to give only two valence electrons because of the stability of half-filled and filled *f* orbitals which would be achieved in these instances. Compounds of europium(II) and ytterbium(II) are well characterized.

The decrease in size within a period is not always consistent, but there are some regularities which are significant. The decrease in size within a period is greatest between the alkali and alkaline earth metals and less for the other representative elements. The differences in size become smaller toward the ends of the periods. The size decrease is small within the transition series, again becoming smaller toward the ends of the series. The smallest decrease to be found in any series of more than a few elements is to be found in the inner transition series. Thus, the decrease in size is most pronounced as *s* electrons are added to a shell, and becomes progressively smaller for *p*, *d*, and *f* electrons. This is the order of decreasing "penetration" of the respective orbits.

Although the contraction from one element to the next in the lanthanide series is very small, the effects are very pronounced since it extends through 15 elements in the same family of the periodic table. As a direct result of the lanthanide contraction the atomic radius of hafnium is slightly smaller than the radius of zirconium. The lanthanide contraction continues to affect the size and properties of the elements beyond hafnium, but to a diminishing extent for each successive element. Another very striking result of the lanthanide contraction is the fact that yttrium is intermediate in size between dysprosium and holmium and is difficult to separate from these elements. However, the nuclear charge has to be increased by nine units before the size of one of the lanthanides is reduced to approxi-

[1] YOST, D. M., H. RUSSELL, JR., AND C. S. GARNER, "The Rare Earth Elements and Their Compounds," John Wiley & Sons, Inc., New York, 1947, p. 53.

[2] MOELLER, T., "Inorganic Chemistry," John Wiley & Sons, Inc., New York, 1952, p. 146.

[3] The atomic, ionic, covalent, and van der Waals radii referred to in the following discussion are those summarized from various sources by Moeller; see Ref. 2, Chap. 5.

[4] HÜCKEL, W., "Structural Chemistry of Inorganic Compounds," translated by L. H. Long, Elsevier Publishing Co., Inc., New York, 1950, p. 244.

mately that of yttrium. If we compare scandium and yttrium, the size difference is much greater than that between yttrium and lanthanum. In spite of the greater difference in size between scandium and yttrium, only two units need be added to the nuclear charge of yttrium to give an atom (Nb) considerably smaller than scandium if the electrons added are *d* instead of *f* electrons. The pronounced contraction in a transition series causes the only other instance of a decrease in size with increasing atomic number in a family. The covalent radius of gallium is slightly smaller than that of aluminum although there are only ten elements between calcium and gallium, representing the filling of the *3d* orbitals.

The size change in the lanthanide series is very small, but the differences in chemical properties, although slight, are enhanced by the relatively high charge on the ions. For the same size difference the differences in chemical properties are greater for tripositive ions than for ions of lower charge. The relative differences can be seen by comparing values of ionic potentials (charge/-size) for the same size difference but different charges.

JOHANNES DIDERIK VAN DER WAALS

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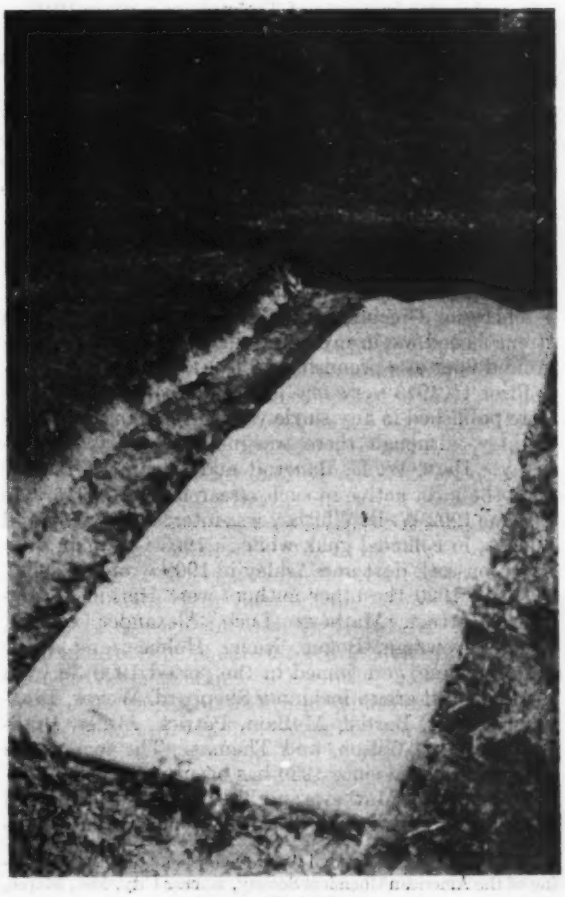
BORN at Leiden on November 23, 1837, van der Waals studied at the University there from 1862 to 1865. He then taught physics at Deventer and The Hague. His doctorate was awarded in 1873 and his dissertation "On the continuity of the gaseous and liquid states" attracted much attention. It was subsequently translated into English, French, and German. This topic was the *leitmotif* of all his important work.

He is best known for his improvement of the equation of state, taking into account the attraction between the particles of the gas and their own proper volume. In other words, the internal pressure of the gas is greater than the observed pressure by the amount a/v^2. He calculated the pressure inside a drop of water to be about 10,000 atmospheres. The second factor responsible for the deviation from the ideal gas law was introduced in the well known correction $(v - b)$. The most important development of this work was the van der Waals law of corresponding states, which enables the operator to calculate the state of any gas or liquid at any temperature and pressure if the state at the critical temperature is known.

The Nobel Prize was awarded to this great theoretician in 1910 "for his work concerning the equation of state of gases and liquids." In subsequent studies he found that b varies with temperature and Clausius found that a is not constant for a given material but varies with temperature. However, the van der Waals equation was a most valuable approach to a very difficult problem and it has been a great aid in the liquefaction of gases and the theory of the modern freezing technique.

Van der Waals died at Amsterdam on March 9, 1923, and is buried there. The plain stone covering his grave is already quite weather-beaten and the inscription is becoming hard to read.



Van der Waals' Grave

THE GROWTH OF COLLOID CHEMISTRY IN THE UNITED STATES[1]

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IT WAS heart-warming to be selected as the first recipient of the Kendall Company Award in Colloid Chemistry, for I labored long—and early—in the vineyard. I feel certain that this honor comes to me, in part, as a recognition of my pioneering efforts in this field.

As long ago as 1910 I gave some laboratory instruction in the preparation of colloids (the first in this country) at Earlham College, and in 1913, bursting with enthusiasm but very inadequate knowledge, I published a sixteen-page review of the general subject in *School Science and Mathematics*.

To the best of my knowledge the second institution to give considerable attention to colloid instruction was Massachusetts Institute of Technology early in 1916.

My first colloid research paper, "Electrostenolysis," published in 1914, got in by the back door under cover of Freundlich's insistence that "Capillarchemie" was a better name than "Kolloidchemie." The theme of this modest paper was that certain metals and metallic oxides could be deposited by a direct current of electricity in very fine capillaries placed between the electrodes.

While teaching at Earlham I listened to a lecture on colloid chemistry by Wolfgang Ostwald, then visiting America, and had stimulating talks with Martin H. Fischer in Cincinnati. These two able chemists strengthened me in my determination to get in on the ground floor of a promising subject.

Prior to 1915 very few papers on colloid chemistry were published in any single year in the journals of this country, although there was much activity in Germany. Here, W. D. Bancroft and Martin H. Fischer were the most active in such research before 1915. As early as 1902 W. R. Whitney was interested, briefly and quietly, in colloidal gold, while in 1903 Cushman published on rock dust and Ashley in 1909 wrote on soils.

Up to 1920 the other authors were Harkins, Langmuir, Gortner, Mathews, Loeb, Alexander, Spence, Brigge, Newman, Bogue, Nagel, Holmes, and a few more. These were joined in the period 1920–30 by a distinguished group including Sheppard, Weiser, Bingham, Taylor, Bartell, McBain, Patrick, Miller, Bradfield, Hauser, Wilson, and Thomas. The increase in papers published since 1930 has been phenomenal.

In 1923 J. H. Mathews and I planned the first Colloid Symposium and, with the aid of an enthusiastic committee, made it a reality, at the University of Wisconsin. The success of this meeting (and its monograph) inspired other groups in various fields to follow suit.

NATIONAL RESEARCH COMMITTEE CAMPAIGN

In 1919 the National Research Committee appointed me chairman of its Committee on Colloid Chemistry, a position that I held for six years. At the request of this committee, in 1921 I wrote the first laboratory manual of colloid chemistry used in this country (three editions). Later I wrote a small text, but there were other, better ones available.

Later I contributed chapters to "Medical Physics," "Collier's Encyclopedia," and the comprehensive books by Alexander and by Bogue.

The Committee wished to spread the gospel in every way possible, so some of us were urged to lecture on our subject whenever invited. I did more than my share, for I addressed a large number of sections of the A. C. S. and spoke at nearly all our larger universities as well as at eight universities in Europe, all the time learning more than I taught.

My own research dealt with dialysis, gels, silicic acid gels, silica gels, catalysts, adsorption, emulsions, and some odds and ends. Finally, in a very logical way, I moved over into the vitamins and biochemistry in general.

DIALYSIS

Soon after moving to Oberlin in 1914 I published a paper on "Washing precipitates for peptization" and a note on "An inexpensive dialyzer." Dialysis seems to have held my fancy, for I came back to it from time to time. For my laboratory manual I developed the idea of "hot dialysis"—as faster than the usual method. With A. L. Elder in 1931 a paper was published on "A new cell for electrodialysis." This device speeded up removal of ionic impurities. Again for the manual, I introduced the use of artificial sausage skins in dialysis.

Of more interest to biologists was my paper, "A practical model of the animal cell membrane," 1939. In this work a membrane (quickly and cheaply prepared) permitted passage of either water-soluble or oil-soluble material, quite similar to the cell walls of animal bodies.

GELS

Gels (or jellies) occupied my attention for several years. Three papers, 1916, 1918, and 1919, with Rindfuss, Arnold, and Fall, dealt with the peptization, dialysis, and gel formation of ferric arsenate and ferric

[1] Presented as the Kendall Award address at the 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

phosphate. The ferric arsenate jelly was beautiful and tempting but obviously had no future as a table jelly. "Jellies by slow neutralization," with Paul H. Fall, 1919, developed the theme that when quick mixing of two solutions yields only a gelatinous precipitate, slow mixing by diffusion through a membrane may yield an excellent jelly.

In the first "Colloid Symposium Monograph," 1923, I published a somewhat general paper, "Gel formation," in which I offered the "brush-heap" theory of gel structure. This resulted from the observation that many beautiful gels were composed of minute crystals with adsorbed and entangled liquid. Also in this paper was the observation that addition of various dehydrating agents to pectin sols caused formation of good pectin jellies.

"The influence of a second liquid upon the formation of soap gels," with R. N. Maxson, 1928, brought out the fact that although anhydrous alkali soaps in general are dispersed with difficulty in hot solvents such as turpentine and benzene, they readily form sols when a relatively small amount of water, oleic acid, or similar polar solvent is present. There are narrow limits to the percentage of polar additive. On cooling, gels (not of long life) are formed, showing increased solvent holding power. "Silicic acid gels," 1918, was the first of a long series of related papers dealing with hydrated silica, dry silica, adsorption, and catalysis. Contrary to previous belief, it was shown that at high concentrations of the acid mixed with sodium silicate gels do form. The dehydrating influence of nonionized molecules of the acid is the determining factor in time of set.

"The formation of crystals in gels," 1917, used the theory that the influence of gels on crystal formation is largely that of regulated diffusion of reacting substances. Although silicic acid was generally used in the experiments, fine powders of sulfur, etc., also served, thus explaining many geologic phenomena. Basic silicic acid gels permitted formation of crystals not possible in the usual acid gels. Gold salts in an acid gel (made with dilute sulfuric) were reduced by inward diffusion of oxalic acid to yield gleaming crystals of gold.

In the next paper, "Rhythmic banding," 1918, controlled conditions permitted formation of beautifully colored bands of colloidal gold, or sharp bands of copper chromate, or of basic mercuric chloride, etc. A new theory of these "Liesegang rings" was advanced.

"The vibration and syneresis of silicic acid gels," 1919, with Kaufman and Nicholas, described the special preparation of silicic acid gels which, half-filling a test tube, vibrated musically on sharp tapping of the tube. They vibrate as rigid solids, rigid because of adhesion to the glass and a great tendency to contract. In vaseline-lined test tubes such gels contracted visibly and pulled away from the walls. A fascinating stunt was tapping a pint milk bottle less than half-filled with the gel. The resulting sound was reminiscent of cathedral bells.

SILICA GELS

The general interest in Patrick's "silica gel" led us at Oberlin into certain experiments that resulted in a paper, "A new type of silica gel," 1925, with J. A. Anderson. We added a solution of ferric chloride to a solution of sodium silicate and obtained as a gelatinous precipitate a molecular mixture of hydrated ferric oxide and hydrated silica. After drying it to a rigid structure we dissolved out the ferric oxide with dilute hydrochloric acid. After washing and drying, a very porous, chalk-white gel of pure silica (slightly hydrated) resulted. In the next paper, "Increasing the internal volume of silica gels by moist heat treatment," 1926, with Sullivan and Metcalf, we checked the initial drying at 60 per cent water content, allowed the partly dried gels to sweat or synerize for a week or two in closed vessels, and then boiled them for a few hours in dilute acid before washing and final drying. Structure was set to a noncollapsing state so that capillaries resulted both from later loss of water and from removal of ferric oxide (as ferric chloride).

From a stream of air saturated with benzene vapor at 30°C. the Patrick type of silica gel adsorbed 32 per cent of its own weight, while our best heat-treated gel adsorbed 126 per cent. However, each has its advantages and disadvantages.

CATALYSTS

It was obvious that such a porous solid could serve as effective support for active catalysts, platinum, for example. A paper, "Platinized silica gels as catalysts for the oxidation of sulfur dioxide," 1929, with Ramsay and Elder, resulted. A high degree of efficiency was obtained.

About this time Jaeger announced a promoted vanadium catalyst rather crudely mixed with a silicious support. We sought to improve this product by mixing solutions of potassium metavanadate and ferric chloride to obtain a precipitate which we peptized, or colloidally dispersed, with sufficient excess of ferric chloride. This colloidal solution was then added to sodium silicate solution to obtain a precipitate composed of catalyst, promotor, and silica support—all molecularly mixed.

After proper drying and testing at 500°C. with a gas flow of 8 per cent sulfur dioxide, an efficiency of 98 per cent was observed. Details are given in the paper, "Vanadium compounds as catalysts for the oxidation of sulfur dioxide," 1930, with A. L. Elder.

Since the usual precipitation of catalysts throughout porous solids may be far from uniform it seemed advisable to try to secure uniformity by first soaking the solid in a solution of the salt desired, salts of platinum, iron, etc., drying, admitting a suitable water-soluble gas (NH_3, H_2S, etc.), and finally immersing the porous solid containing the dry salt and adsorbed gas in water. Delayed reaction then resulted. The idea of delayed reaction was extended so as to reduce platinum salts by carefully moistening the dried gel containing sodium chloroplatinate with a formalin solution. Fortunately, reduction in this instance is slow at room temperatures. Upon raising the temperature to 100°C. reduction is completed. ("Uniform distribution of catalysts in

porous solids," 1928, with R. C. Williams, was the resulting paper.)

My final excursion into the field of catalysis followed isolation of vitamin A in the Oberlin laboratories. Other workers had observed orange and red color bands while filtering solutions of fish-liver oils through columns of fine white powders. They could not prove their suspicions that these bands were due to changes in the vitamin A known to be present. As soon as Corbet and I obtained the vitamin without confusing impurities—a great advantage for us—we tried it in seven different solvents on seven different adsorbents. Catalytic formation of orange-red bands was observed in several instances. Evidently care is called for in such chromatographic treatment of sensitive organic compounds. Details are given in "Catalytic effects of porous powders on pure vitamin A," 1939, with Ruth Corbet.

ADSORPTION

Bancroft once told me, "Adsorption is the heart of the subject." With porous gels at hand, it was natural for me to delve in this field. I questioned Freundlich's extension of Traube's rule to nonaqueous solution, that adsorption of organic substances from aqueous solution increases strongly and regularly as we ascend the homologous series.

Since Freundlich's studies dealt with carbon, a nonpolar solid, and water, a polar liquid, it occurred to me that the order of adsorption in a homologous series of fatty acids must be reversed when the acids are adsorbed on silica, a polar solid, from toluene, a nonpolar liquid. This surmise proved to be correct, as shown in a paper, "The reversal of Traube's rule of adsorption," 1928, with J. B. McKelvey.

"The removal of sulfur from petroleum distillates," 1932, with Elder and Beeman, was a report on experiments with silica gels and with our own type of silica gels impregnated with copper sulfide. With careful preparation, adsorption was high. In the above paper an improved form of the sulfur lamp for the oil industry was described.

Thiophene-free benzene has some importance in the manufacture of certain dyes, so it seemed worth while to inquire why treatment of ordinary benzene with anhydrous aluminum chloride had never proved successful. Reaction alone was not enough, for the colored product was somewhat soluble and at high temperatures removal by adsorption was poor. We secured complete removal of thiophene by successive treatments at about 35°C., a temperature high enough for reaction yet sufficiently low for effective adsorption. The details are given in the paper "Removal of thiophene from benzene," 1934, with N. Beeman.

My determination to attempt the isolation of fat-soluble vitamin A seemed to make necessary a preliminary research, "The adsorption of fats from volatile solvents," 1930, with J. B. Thor. Polarity influence was evident.

The next effort, "Comparative studies on the adsorption behaviors of crude vitamin A, carotene and cholesterol," 1933, with Lava, Delfs, and Cassidy, emphasized the importance of polarity in solvents and in the adsorbents used, carbon, our silica gel, and eight types of alumina. A by-product of this research was "The isolation of carotene," 1932, with H. M. Leicester.

Near, but not complete, success in isolation of vitamin A from the nonsaponifiable fraction of fish-liver oils was reported in the paper, "Preparation of a potent vitamin A concentrate," 1935, with Cassidy, Manly, and Hartzler. In Europe, Karrer had been reviving use of adsorption columns, as described by Tswett in 1906, so I adopted and varied this valuable technique for separation of impurities from vitamin A. It is probable that I was the first to introduce chromatography into this country. Karrer extruded the wet columns and cut them into sections, while I preferred to wash the adsorbed bands through, collecting the filtrate in fractions. Carbon had not been reported for Tswett columns, partly because it obscured the colors of bands and, in vitamin A research, had caused serious oxidation loss. The latter objection was removed in the Oberlin laboratory by thorough removal of air in carbon activation and replacement with nitrogen.

Filtering a solution of a concentrate, first through carbon and then through magnesium oxide, we obtained finally a much more potent concentrate of vitamin A than any previously reported from Europe. However, since we realized that probable catalytic effects of the porous powders would prevent isolation of a pure product, the plan of attack was greatly changed. Crystalline vitamin A containing one molecule of methyl alcohol of crystallization was obtained, as reported in "The isolation of crystalline vitamin A," 1937, with Ruth Corbet. Later, other workers recrystallized this product from methyl formate without any solvent of crystallization.

EMULSIONS

My interest in emulsions began rather early and was heightened by Bancroft's adsorption-film theory. A series of papers resulted: "Gelatin as an emulsifying agent," 1920, with W. C. Child; "Cellulose nitrate as an emulsifying agent," 1922, with D. H. Cameron; "Polar emulsifying agents," 1925, with H. A. Williams; "Chromatic emulsions," 1922, with D. H. Cameron; "Emulsion films," 1925; "Iodine as an emulsifying agent," 1925; and an extended review of my work in a French journal made up the list.

The beautiful and spectacular chromatic emulsions with all the colors of the rainbow excited most interest. In this research it was shown that transparent emulsions result when the refractive index of the two liquid phases is the same while the optical dispersive power is also the same. However, when the optical dispersive power of one phase is much greater than that of the other, beautiful color effects are obtained.

DRY BOX TECHNIQUE

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STUDIES of the chemical and physical properties of easily hydrolyzed materials have always been hampered by the experimental difficulties of preparing and transferring samples in the absence of water. In the case of such substances as zirconium and hafnium tetrachlorides, even momentary exposure to air results in appreciable changes in composition. The most precise work on such material has always involved indirect sampling techniques.[1, 2, 3] Considerable time and effort went into the design and construction of a "dry box" by means of which sampling of easily hydrolyzed materials could be made to approach the "ordinary" techniques. The box in use was made to our specifications by the Pickard Roofing Co. of Durham, North Carolina, at a cost to us of $616.00. Design details are the work of Mr. A. R. Bennett, of the departmental staff.

Scale details of the box are shown in Figure 1. One-sixteenth-in. stainless steel was used. All joints are welded and soldered over to insure airtightness. The bottom and back are braced by riveting to angle iron (not shown in drawing), and covering the rivets with solder. The bracing is necessary to prevent buckling of such large surfaces of steel. A double fluorescent tube bracket (containing additional 110 a.-c. outlet) is mounted on the inside of the top. The small chamber on the right end of the dry box is a predrying chamber.

[1] HONIGSCHMID, O., ET AL., *Z. anorg. Chem.*, **139**, 293 (1924).
[2] HONIGSCHMID, O., ET AL., *Ber.*, **58**, 453 (1925).
[3] VENABLE, F. P., AND J. M. BELL, *J. Am. Chem. Soc.*, **39**, 1598 (1917).

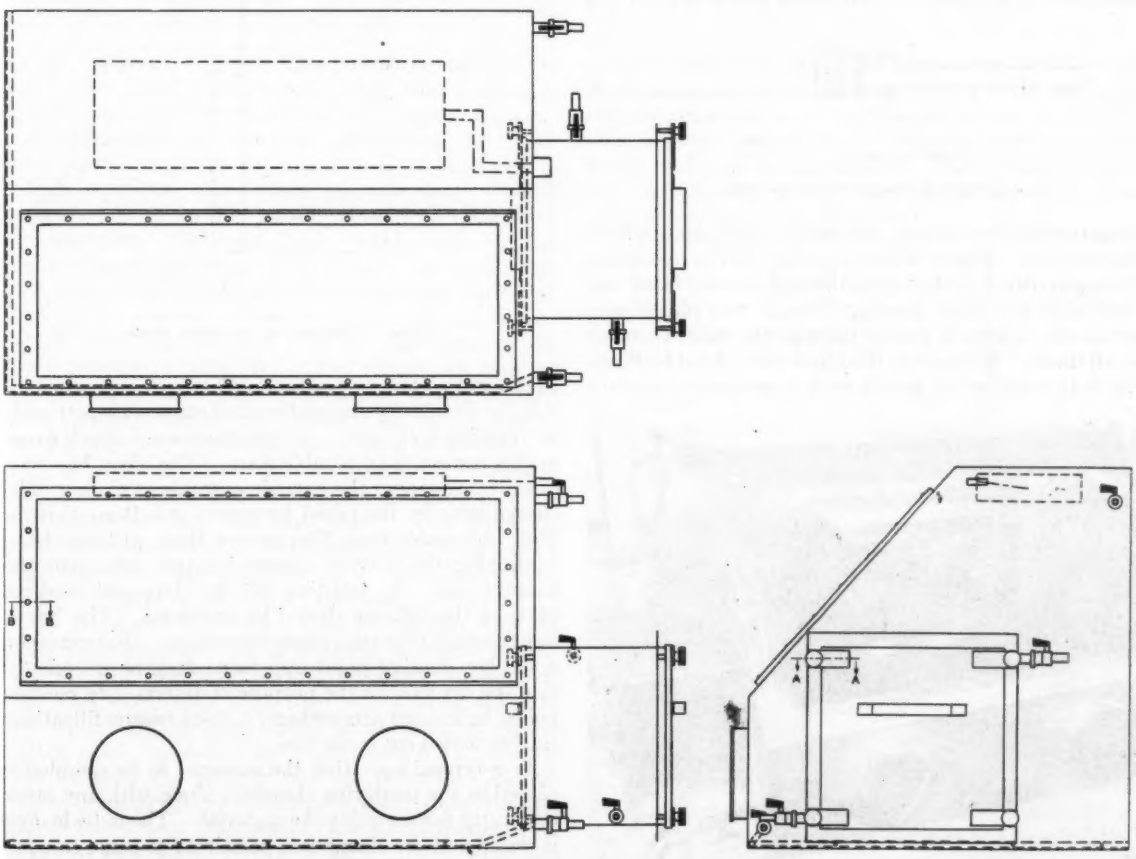

Figure 1. Dry Box

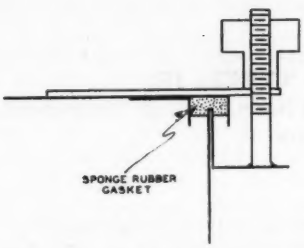

Figure 2. Detail of Predrying Chamber Seal

Provision is made for sweeping both chambers independently with some dry, indifferent gas. The outer and inner doors of the predrying chamber are interchangeable and the seal detail is shown in Figure 2. The interior of the box is viewed through a large safety-glass window, sealed as shown in Figure 3. Figures 2 and 3 are sectioned from Figure 1 as indicated. This window is removed only for major operations, whereas the predrying chamber doors are opened whenever materials are removed from or introduced into the main dry box. Special Neoprene dry-box gloves (obtainable from Safety Equipment Dist. Co., Knoxville, Tenn.), mounted on the ports by means of stainless steel slip

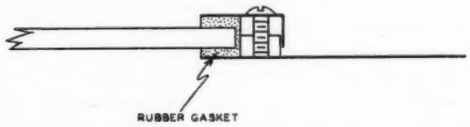

Figure 3. Detail of Window Seal

rings over rubber gaskets, are used to manipulate within the dry box. Figure 4 shows the dry box in operation. Nitrogen, dried by bubbling through concentrated sulfuric acid and then passing through two phosphorus pentoxide towers, is passed through the main chamber at all times. If the air in the box is to be dried by flushing in this matter, at least a week is necessary to establish equilibrium. Dishes of phosphorus pentoxide are kept in the box also. The nitrogen enters the box through perforated stainless-steel tubes along the bottom of the box and leaves via the valve in the upper corner. It is then passed through a dew-point meter, by means of which the humidity in the box is measured. After passing through the dew-point meter the gas is exhausted to the atmosphere through a tower of calcium chloride. It is desirable to maintain a dew point of about −50° in the box. Under such conditions, samples of zirconium tetrachloride may be weighed on open weighing pans on the analytical balance in the box without detectable hydrolysis. It is of interest to note that

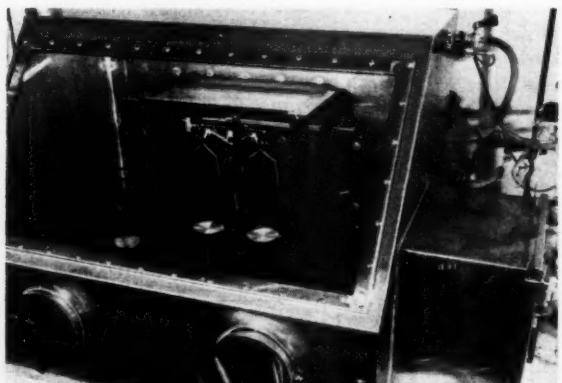

Figure 4. Dry Box Ready for Use

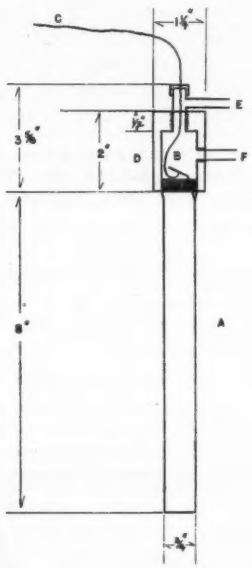

Figure 5. Diagram of Dew-point Meter

electrostatic charges persist on glassware and other insulators in this dry atmosphere and cause serious trouble in weighing accurately. Pyrex glassware is much worse in this respect than Kimble ware. The effect has been observed to render the balance unstable at times. The charge may be dissipated by means of a Reco Neutra-Stat, obtainable from Phipps and Bird, with the head containing the activity source located right over the balance pan. In addition the dry box and working parts of the balance should be grounded. The box is large enough to permit many operations. For example, a Fischer melting point apparatus may be introduced into the dry box for the purpose of determining melting points in an inert atmosphere. Also pressure filtrations can be carried out in the box.

In a typical operation the material to be sampled is placed in the predrying chamber, along with any other apparatus for sampling the material. The outside door is closed and the chamber is permitted to come to equilibrium. This is always hastened by including a dish of fresh phosphorus pentoxide. This equilibration may

take as much as two hours. The inner door is opened, working through the gloves, and the materials moved into the box. The inner door is then closed. Once safely in the dry box the material is transferred to ordinary weighing bottles, from which containers it may be sampled, using the analytical balance. Samples are removed from the box by opening the inner door, moving materials into the predrying chamber, closing the inner door and opening the outer door.

The dew-point meter is shown in Figure 5. The long copper tube A is immersed in a dry ice acetone Dewar and a polished copper surface B is silver-soldered to A. The temperature is recorded by a thermocouple C spotted under the center of the surface. The top D is of Lucite, threaded to fit the large copper tube and the two smaller copper tubes E and F. The exit gas from the dry box enters at F and leaves at E. The temperature at which dew is first observed on the polished copper surface is read as the dew point.

ACKNOWLEDGMENT

The author gratefully acknowledges the financial support of the U. S. Atomic Energy Commission, which made possible the fabrication of the dry box.

A PHOTOTUBE CIRCUIT WITH TRANSISTORS

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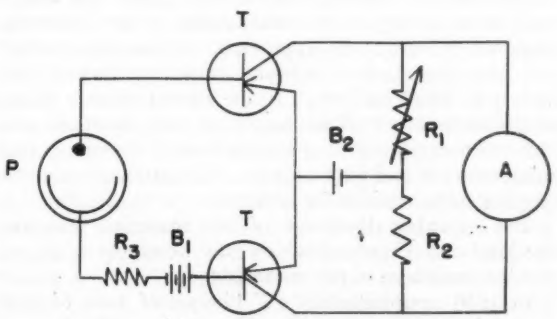
It is commonly known that vacuum phototubes yield such small photocurrents that amplification is desirable to avoid circuits containing fragile and expensive galvanometers. Vacuum phototubes are thus more complicated for use in colorimeters than photovoltaic selenium cells, which generate large enough currents not to require amplification under ordinary circumstances. However, photovoltaic cells require low-resistance meters in order to give currents linear with light intensity and they do not have the variety of response to portions of the spectrum that can be obtained from the different vacuum phototube types. Even though vacuum phototubes require an external power supply, their greater versatility would warrant more extensive use in colorimeters if the circuit complications of a vacuum tube amplifier could be avoided.

In a recent article[1] a current-amplifying transistor circuit so compact that it could be mounted inside a microammeter case was described. With matched junction transistors of the Raytheon CK-721 type and a high impedance input, this circuit, in effect, converted a 25-microampere meter into a 1-microampere meter.

We employed this circuit (see the figure) with an RCA 929 phototube and "B" battery to supply the input current. We expected, and did obtain, meter readings that were larger than the corresponding currents (for equal light intensity) from an unamplified photovoltaic cell. Instead of the expensive CK-721 transistors we used the cheaper but less powerful CK-722. It was necessary to do some trial-and-error experimenting to find a pair that would balance adequately. A balanced pair would give zero dark current when the variable resistance, R_1 in the figure, was equal to the fixed resistance, R_2. The best pair we could find gave current amplification of nearly eight times; *e. g.*, a 20-microampere current read 150 microamperes on our meter (a Heathkit multimeter). With better transistors considerably greater amplification should be possible, according to the literature.[1]



Phototube Circuit with Transistors

A, 150-μa. meter. R_1, 5000-ohm variable resistor. R_2, 4300-ohm resistor. R_3, 1-megohm resistor. B_1, 45 v. B_2, 1.34 v. *T*, CK-722 junction transistors. *P*, RCA 929 phototube.

Since the cost of this amplifier, exclusive of meter, is about $10 and the construction in a breadboard fashion is very easy, the unit might be useful in a colorimeter. Such a colorimeter would be superior in sensitivity to the barrier layer cell circuits commonly available, and also would not require a meter of critically important low resistance.

[1] Starke, H. F., *Radio and Television News*, **50**, 82 (1953).

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

RAW MATERIALS FOR AMERICAN INDUSTRY[1]

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In the beginning course in chemistry attention is usually given to a number of industrial processes by which raw materials are converted into useful consumer products. Extraction of metals from ores, refining of petroleum, production of lime, and the manufacture of cement and glass are examples. Such items serve to emphasize the importance of chemistry to industry and to mankind in general. Usually only casual reference is made to the sources of raw materials, to the quantities required to support American industry, and to the present and future problems of supplying adequate quantities.

It seems to the author that it is desirable to broaden the treatment of raw materials in the chemistry course for at least two reasons. In the first place, raw materials have a very direct relationship to the American standard of living. An appreciation of this relationship can give the student a better understanding of the society in which he lives. In the second place, a study of problems involved in supplying raw materials will indicate many interesting applications of chemistry and other sciences and may suggest to the student some intriguing opportunities for a career.

The following discussion of raw materials suggests the kind of background which may be useful in an expanded treatment of raw materials.

In 1950 approximately 2.7 billions of tons of raw materials were consumed in this country. That is an average annual consumption of 36,000 pounds, or 18 tons, per capita. Those 18 tons included more than seven tons of fuels, five tons of construction materials, and nearly three tons each of agricultural products and minerals. No other people at any other time in history have ever developed such a consumptive capacity. Since standards of living are measured by use of materials, it follows that no other people have ever had such a high standard of living. The fact that the people of the United States, with about 10 per cent of the population of the free world (*i. e.*, excluding those areas dominated by the Soviet Union) consumes approximately one-half of the total production of raw materials, indicates the vast difference that exists between the standard of living in this country and in many others.

There can be little doubt that the development of an economy which requires huge quantities of raw materials is closely related to the availability of those materials. Few, if any, areas of the earth equal in size to the United States possess such large quantities of so many varieties of raw materials. Not only has the abundance of raw materials encouraged prodigious use but also it has led to the rather commonly held view that the resources of this country are virtually unlimited. It is true that a few far-sighted people raised their voices to challenge this view many decades ago. They had little effect in changing the attitudes of the average citizen. As a nation, we have subscribed to the idea of an expanding economy, which means quite simply an ever-increasing consumption of raw materials.

There are two major reasons for the steadily increasing demands for raw materials in this country. One is our rapidly increasing population. For example, since the last census in 1950 our population has increased by approximately 10,000,000. Thus, just to maintain the standard of living of 1950, there was needed about 175 millions of tons of raw materials more than was consumed in 1950. Actually the standard of living is not fixed in this country but rises steadily. For many years, the average per capita income has been increasing, measured in dollars of fixed value. This is the second reason for increasing demand for raw material. As people earn more, they spend more for homes, for automobiles, for household gadgets, for clothing, all of which require raw materials for their manufacture.

There seems to be no immediate prospect that the population of the United States will cease to grow nor is there any apparent desire on the part of business, in-

[1] Presented at the 276th Meeting of the New England Association of Chemistry Teachers, Emmanuel College, Boston, Massachusetts. The paper is a résumé of ideas accumulated during a year of study and travel supported by the Ford Foundation.

dustry, and the general public to abandon an expanding economy with the attendant increasing standard of living. Thus, we can expect steadily increasing demand for consumption of raw materials. It has been estimated that the combined effects of population growth and increased average income will create, by 1975, a demand for about 1 billion tons more of raw materials than in 1950.

The question naturally arises as to how long skyrocketing demands for raw materials can be met. During the last decade there has been serious consideration of this question, and as might be expected there is wide difference of opinion. On the one hand there are those who feel that the future is gloomy indeed unless means are found to limit the growth of population and to level off the standard of living. At the other extreme, there are those who feel that problems which may arise are largely technical in nature and are capable of solution through scientific research.

As a basis for predictions about the future of raw materials supply, it is helpful to review the past. In spite of enormously rich resources of raw materials, the United States has never been completely self-sufficient. However, up to about 1940, the United States always produced more raw materials than it consumed. That is to say, the value of export of raw materials always exceeded the value of imports. About 1940 production and consumption were approximately equal. Since 1940 our consumption of raw materials has regularly exceeded our production. In 1950 the deficit of production was about 10 per cent. By 1975 the deficit will probably reach 20 per cent.

It is easy on the basis of such comparisons to arrive at the entirely erroneous conclusion that the United States is rapidly running out of resources of raw materials and is becoming a have-not nation. Actually, the United States is the world's largest producer of a number of essential raw materials. Furthermore, in spite of the depletion of many of the richest deposits of raw materials, the discovery of new deposits and improvements in technology have made it possible to increase the production of some raw materials steadily. Petroleum is a notable example. The discrepancy between production and consumption is in part owing to the fact that it has been impossible to step up production to the same extent that demand has increased. In part, the discrepancy is due to an entirely different cause. Not only has the total demand for raw materials increased but also industry now demands a much greater variety of raw materials than formerly. The chemist is perfectly familiar with the fact that substances such as titanium which were laboratory curiosities a few years ago are now needed to the extent of thousands or tens of thousands of tons annually. Some of the raw materials for which demand has developed recently are not available from domestic deposits.

Discussion of the changing pattern of supply for a number of specific raw materials will serve to emphasize the general pattern already set forth. The discussion will be restricted to materials which are extracted from the earth, *i. e.*, ores, minerals, and fuels.

ORES

Iron ore is a basic raw material for an industrial economy. This country has many large and widely scattered deposits. No doubt our industrial development has been closely related to the availability of tremendous quantities of high-grade ore, particularly from the Lake Superior iron ranges. The original Lake Superior deposits contained such high-grade ore that it could be charged directly into blast furnaces. In spite of the original enormous size of the Lake Superior deposits, they have been depleted to the extent that virtually all the ore now shipped receives some treatment to up-grade the quality. Great quantities of low-grade ore, called taconite, still exist in the Lake Superior region. Much progress has been made in developing methods of beneficiating taconite so that it will certainly become an important source of iron. In spite of technical developments, it has been necessary for the United States to turn to foreign sources for a part of its iron ore supply. The figures on iron ore production and consumption for 1953 illustrate particularly well the point made earlier that our productive rate cannot keep pace with our consumption. In 1953 we produced 133.5 million tons of iron ore from domestic mines—the highest production on record. During the same year we imported 12.4 million tons, also the largest import on record. The imported ore came from 19 countries, with Chile, Sweden, Venezuela, Canada, Peru, and Liberia supplying the major portion. Early in 1954 the first shipments of ore were received in this country from new mines in Venezuela. It is reported that the first shipments of ore from new mines in Labrador will be made in the fall of this year. Consequently, it can be expected that the years ahead will see a steadily increasing flow of iron ore into this country from foreign sources.

Ores of the alloying agents for use in making steel are largely absent in this country. Manganese ores are used to the extent of one and one-half million tons per year or more. Of this quantity, only 5-10 per cent are supplied from domestic sources. We do have considerable quantities of low-grade manganese ores, but in spite of a great amount of research, methods are not yet available for using them economically. The largest known deposits of high-grade manganese ores are in the Soviet Union. Formerly, we imported large quantities from this source. More recently, we have had to rely on ores obtained from India, South Africa, Brazil, and numerous other countries.

Nickel ores are almost entirely lacking in this country. It is fortunate that the largest and richest known deposits are in Canada. Even in times of war this source is available by land routes. Since the Canadian deposits are the source of about 80 per cent of the world supply of nickel, in times of industrial activity the supply is usually short. That fact has stimulated efforts to develop other sources of nickel ores, especially the lateritic ores found in tropical areas. Considerable quantities of these ores, which are relatively complex

and low-grade, are found in Cuba, where a large plant for extracting nickel was constructed during World War II. Further improvements in the processing of these ores must be made before lateritic ores can be considered an important and economical source of nickel.

Chromium ores of high grade are in extremely limited supply in this country. There are low-grade deposits which can be utilized in times of war when cost is of little moment. Normally, we import nearly all of our needs, amounting at present to about a million tons of chromium ores annually. These ores come from Turkey, the Philippines, South Africa, and numerous other countries.

Much the same story can be told for other alloying agents, such as tungsten, vanadium, cobalt, and niobium. At best, the United States can supply only a part of its present requirements. In only one alloying agent, molybdenum, are we completely self-sufficient.

The nonferrous metals follow much the same pattern as the ferrous metals. Only magnesium can be produced from domestic sources of raw materials in sufficient quantities to supply all needs. Lead, zinc, and copper were formerly exported in considerable quantities. Today we import about one-third of our requirements of each. In each case, we still remain very large producers, but production simply has not been able to keep pace with demand. Copper production in this country illustrates how improvements in mining and ore processing can be an aid to continued high production. Only a few years ago ores of copper averaging less than 2 per cent of metallic content were considered unprofitable to mine. At the present time a large part of the copper production in the United States comes from ores containing 1 per cent or less of metal. Yet no important change in the price of copper has been necessary.

Much of the aluminum metal used in the United States comes from ores imported from Jamaica and from Surinam. Domestic deposits of bauxite, which is the only ore of aluminum used at the present time, are limited in extent and of rather poor quality. In spite of much research, no economical methods have been devised for extracting aluminum from various minerals which are much more abundant than bauxite.

FUELS

The story of fuels is a much happier one in terms of domestic supplies. Our reserves of coal are enormous, although it seems unrealistic to state, as is frequently done, that they are large enough to supply all possible needs for a thousand or more years. Much of the coal is in deposits which are entirely uneconomical to mine by any presently devised methods. In spite of the availability of enormous quantities of coal, types which are suitable, as mined, for making metallurgical coke have been seriously depleted. Much coal now used for coking requires preliminary treatment. While there seem to be no insuperable technical difficulties in upgrading and blending available types of coal for making coke, such treatment tends to raise prices, a factor which has an effect similar to actual shortages. That is, high prices may change the pattern of use of raw material nearly as effectively as scarcity.

Natural gas is available in tremendous quantities in the United States. Until recently, great amounts of natural gas were wasted for lack of economical uses. The expansion of pipeline facilities to populous and industrialized areas during the last ten years has expanded the market and the consumption enormously. It is the policy of the Federal Power Commission to allow expansion of pipeline facilities into a new area only if proved reserves of gas are available for supplying the demands for twenty years. Thus, it seems that there should be no immediate shortages of this fuel. However, the demand for natural gas not only as a fuel but as a chemical raw material is increasing so rapidly that the price at the source of production is being raised. This might be interpreted as an indication that demand is already tending to exceed supply.

The United States has for many years been the world's largest producer of crude petroleum. In spite of depletion of many oil fields, the petroleum industry has, up to this time, been extraordinarily successful in discovering new deposits, so that known reserves of crude petroleum are now the largest in history. The rate at which petroleum is to be extracted from the earth has an important influence on the total amount that can be extracted. Thus, in spite of our great reserves, it is not economically feasible to extract petroleum rapidly enough to supply our total needs. For a number of years petroleum has been imported, especially from Venezuela and more recently from the Middle East. It seems inevitable that there will be an increasing reliance on foreign sources for petroleum in order to supply our steadily mounting demand for this important raw material.

NONMETALLIC MINERALS

In general, the United States has more adequate supplies of nonmetallic minerals than it does of metallic minerals. Many—for example, salt and limestone—are so abundant as to be practically inexhaustible. For many years the United States has been an exporter of sulfur. During some recent years there have been shortages because the Gulf Coast sulfur deposits were called upon to supply the European as well as the domestic demand. A number of installations have been made to extract sulfur from natural gas, from smelter fumes, or from industrial wastes. While deposits of sulfur minable by the Frasch process are limited and being rapidly depleted, there seems to be no serious problem, unless it be rising costs, to securing an adequate supply in the future from the sources mentioned, or from pyrites.

Phosphate rock is available in large enough quantities to supply forseeable demand for a long time to come. The easily mined deposits in Florida are being depleted rapidly, however, which raises the question of costs when main reliance must be placed on the very large deposits of the Rocky Mountain area.

Potash is a raw material for which the trend in this country is rather unique. Until after World War I we imported almost all the potash which we consumed. The discovery of potash deposits of considerable extent near Carlsbad, New Mexico, and at Searles Lake, California, has made the United States independent of foreign sources. There seem to be ample reserves now known to supply the demand for a great many years.

There are several nonmetallic minerals in which this country is notably deficient. Asbestos is one. Somewhat less than 10 per cent of our needs can be obtained from domestic sources. We produce almost no long-fiber asbestos. Canada is a chief source of supply, although special grades must be obtained from South Africa and Bolivia.

Another nonmetallic mineral which is imported in considerable quantities is fluorspar. This mineral is at present considered essential to certain metallurgical operations. Fluorine compounds are found in phosphate rock in tiny amounts. Because of the great quantities of phosphate rock now used in the production of fertilizers, the total amount of fluorine compounds is large. In the future it may be possible to recover fluorine from phosphate rock for use in the synthesis of fluorspar and other fluorine compounds.

A third nonmetallic mineral which must be imported is sheet mica. This is obtained largely from India. Recent developments indicate that mica can be synthesized in sheets, thus giving rise to the hope that we may eventually be independent of foreign sources.

This brief and incomplete review of specific raw materials indicates two important points. First, maintenance of large-scale production of a number of raw materials has been possible through technological improvements in mining and processing. It is the demonstrated effectiveness of research in bringing about such improvements that is conducive to an optimistic view of the future. Second, the review indicates increasing reliance on foreign sources of raw materials to support American industry.

It is a moot question whether the United States should place increasing reliance on raw materials from foreign sources. In the first place, the rich deposits now available in foreign countries will be subject to rapid depletion as our own deposits have been. In the second place, some difficult problems in international relations, finance, and politics must be solved to allow exploitation of the natural resources in foreign lands. Finally, the trend toward industrialization and higher standards of living in all countries is creating worldwide demands for raw materials. It seems inevitable that the stream of raw materials flowing into the United States will reach a peak some time in the future and then diminish.

In the long run, then, it would seem likely that we must depend more and more upon domestic resources. If we are eventually forced to rely more extensively upon domestic sources of raw materials, a large number of problems must be solved. For one thing, we need to know a great deal more about the raw materials available in this country. Very little indeed is known about the mineral deposits which may be located 1000, 2000, or 5000 feet below the earth's surface. Only within recent years have techniques and instruments been developed for underground exploration. The opportunities for further developments in geology, geochemistry, and geophysics seem to offer intriguing possibilities for careers in these fields.

There is no question that the present trend toward the use of lower grades of raw materials will continue. The task of separating small or even minute quantities of desirable materials from ores demands new techniques of beneficiation if the cost of the desired material is to be kept from becoming prohibitive. Here are fascinating opportunities for the chemist, the physicist, and the engineer.

Some of the most abundant materials on the earth are little used as raw materials. From them it is possible that substitutes may be developed for materials which are scarce. Before this can be done, however, vast new chapters must be written in the knowledge of the properties of substances. An enormous field for chemical and physical research lies in the abundant materials which are of little use at present. In the same materials, too, may reside the key to an abundant life in the future.[2]

There are numerous other possibilities of enlarging and extending the supply of raw materials. More efficient mining methods, better design of structures to require less material, salvage and reuse of materials, and improvements in the efficiency of fuel-using devices are examples. Here again there are challenging opportunities for pure and applied research.

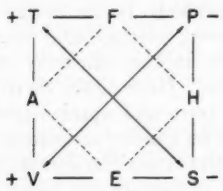
There seems to be general agreement among competent students of the American economy that the hope (some would add *if there is any hope*) for continuance far into the future of the present trends in the consumption of raw materials lies in scientific research. The volume of research required to solve the problems of the future may well prove to be enormous. It seems certain that there will be need for greatly increased numbers of men and women with the finest possible training in science and technology. If that be so, the key raw materials are boys and girls. Teachers of science are the processors who must develop from these raw materials a supply of technically trained products adequate for the demand.

[2] "Resources for Freedom: A Report to the President by the President's Materials Policy Commission," five volumes, U. S. Government Printing Office, 1952, is one of the best single sources of basic information about raw materials. In order to keep abreast of the changes in raw materials' demand and supply, the "Minerals Yearbook," published biennially by the U. S. Bureau of Mines, is helpful. *Chemical and Engineering News* is an excellent source for week-by-week developments.

To the Editor:

Shih-Ching Su's diagram for memorizing four thermodynamic relations (THIS JOURNAL, **24,** 304 (1947)) can be extended to correlate many more thermodynamic equations if they are based on the principle of symmetry of thermodynamic potentials (GUGGENHEIM, "Thermodynamics, An Advanced Treatment for Chemists and Physicists," Interscience Publishers, Inc., New York, **1949,** p. 21). The new diagram consists of eight thermodynamic functions arranged in a square. The order of the symbols can be remembered by means of the following code sentence: "The Free Potential Has Shown Endless Valuable Applications." The notation is that of Lewis and Randall, which is used extensively in most textbooks.

In order to obtain dE as a function of appropriate independent variables, two diagonal lines are drawn toward E, taking the signs corresponding to the symbol of the base of vector,



$$dE = -PdV + TdS$$

In a similar manner are obtained:

$$dA = -PdV - SdT$$
$$dF = VdP - SdT$$
$$dH = VdP + TdS$$

The partial derivatives with variable and independent variable may be obtained from triangular relationship, *e. g.*, ΔSVT,

$$\left(\frac{\partial E}{\partial S}\right)_V = T$$

the variable, V, is situated at the right angle, while the independent variable and answer are at the other apexes. Applying this principle, it follows that:

$$\left(\frac{\partial E}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$
$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$
$$\left(\frac{\partial F}{\partial P}\right)_T = V$$
$$\left(\frac{\partial F}{\partial T}\right)_P = -S$$
$$\left(\frac{\partial H}{\partial S}\right)_P = T$$
$$\left(\frac{\partial H}{\partial P}\right)_S = V$$

The Maxwell relationships can be obtained easily by considering the right triangles with same base, *e. g.*, ΔTVS, ΔPSV:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

The same is true for:

$$-\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

Four other relations may be derived from corners of the diagram:

$$\left(\frac{\partial V}{\partial S}\right)_E = \frac{T}{-P}$$
$$\left(\frac{\partial T}{\partial V}\right)_A = \frac{-P}{-S}$$
$$\left(\frac{\partial P}{\partial T}\right)_F = \frac{-S}{V}$$
$$\left(\frac{\partial S}{\partial P}\right)_H = \frac{V}{T}$$

Another four relations can be obtained by the trapezoid $EATS$, $AFPV$, etc.

$$E - A = TS$$
$$A - F = -PV$$
$$F - H = -ST$$
$$H - E = VP$$

Many other relations, such as chemical potentials, also can be derived, *e. g.*, by considering each side of the diagram,

$$\mu = \left(\frac{\partial E}{\partial n}\right)_{S,V} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial F}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial n}\right)_{P,S}$$

A similar approach based on group theory has been published by Prins (*J. Chem. Phys.*, **16,** 65 (1948)).

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● CHEMISTRY OF THE DEFECT SOLID STATE

A. L. G. Rees, **Chemical Physics Section, Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne. Methuen and Co. Ltd., London; John Wiley & Sons, Inc., New York, 1954. viii + 136 pp. 42 figs. 6 tables. 11 × 17 cm. $2.**

As STATED in the preface, this addition to Methuen's Monographs on Chemical Subjects is designed to stimulate interest and research in the defect solid state, particularly as applied to chemistry. With this objective in mind, the author presents a well organized and interesting account of concepts basic to an area of science involving physics, chemistry, and metallurgy and their application to such important subjects as solid state reactions, oxidation mechanisms, and heterogeneous catalysis.

In the first chapter, which serves as an introduction, the various types of structural defects are discussed, using such well-known examples as the alkali halides, nonstoichiometric oxides, and impurity semiconductors. A comprehensive symbolic formulation for the formation and interaction of defects concludes the chapter. Chapter II (44 pages) is concerned essentially with an outline of the statistical thermodynamic and quantum mechanical methods of approach to the description of defect properties and behavior. The use of physical methods for the experimental determination of structural properties and electronic energy levels associated with defects is the subject of Chapter III. Chapter IV is concerned with the importance of defects in the reactivity of solids and a general discussion of the basic mechanism involved in heterogeneous reactions. Chapter V is devoted to a more detailed consideration of simple dissociation and tarnishing (oxidation) reaction kinetics and mechanisms, while a brief outline of heterogeneous catalysis is given in Chapter VI. In Chapter VII the author stresses the importance of the defect solid state to industry and science and summarizes the problems that must be solved before a comprehensive understanding of the subject is achieved.

The tentative nature of conclusions concerning even the simplest and most exhaustively studied systems, and the need for further research are emphasized throughout the book. While no attempt is made to treat the subject of defect solids comprehensively, a considerable amount of information is presented in a logical manner, with little digression into detailed accounts of the complex, obscure, or controversial issues. The value of the book is enhanced by the frequent use of pertinent examples and illustrations.

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GRAND ISLAND, NEW YORK

● APPLIED ATOMIC ENERGY

K. Fearnside, E. W. Jones, **and** ***E. N. Shaw.*** **The Philosophical Library, New York, 1954. viii + 156 pp. Illustrated. 13 × 19 cm. $4.75.**

THIS almost-pocket-sized book outlines the whole realm of nonmilitary applications of nuclear energy in 147 small pages of text. The authors, associated with the British firm Isotope Developments Limited, are writing for the nonspecialist. In spite of the beautiful clarity of the flowing prose, it is doubtful that the uninitiated layman will feel at home with such eleven-page treatments as that afforded Modern Nuclear Physics in the opening chapter. It would appear to be excellently suited to teachers or students of science who want to find a compact, authoritative, and well organized survey. It is loaded with pertinent examples, yet is unburdened by the details necessary for one working in the field.

The chapter on Nuclear Reactors treats the essential problems in comprehensive fashion, but it falls far short of presenting the present status of successful achievements in the field. This will be apparent particularly to American readers who are well informed on the scientific news from this side of the Atlantic. The third chapter, Preparation and Distribution of Radio-Isotopes, similarly is of limited interest since it is based on the activities of the A. E. R. E. at Harwell. Methods of preparation are similar at "Oakridge," but differences in the scope and mechanics of the A. E. C. program are important The same comment pertains to the chapter on Legal Aspects of Atomic Energy. The concept of security operative in this country is barely alluded to.

The second half of the book accomplishes its job best. The authors organize their admirable survey of the research applications of radioisotopes under the topics: Pure Research, Biology, Medicine, Agriculture, and Industry. The text consists almost entirely of examples, yet the reader is able to see historical developments, appreciate the emphases imposed by techniques and isotope availability, and recognize trends which may lead to widespread applications in the future. The illustrative plates are well chosen. Scientific readers will be glad to find the exposition of results accompanied by satisfying descriptions of experimental techniques. College professors will be pleased by the combination of comprehensiveness and brevity, but will be disappointed by the lack of references to the literature, especially if they should be interested in undertaking experiments themselves. The bibliography is not extensive, nor does it include the best works on the subject available in most American libraries.

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● PROCEDURES IN EXPERIMENTAL METALLURGY

A. U. Seybolt, **Research Laboratory, General Electric Co., Schenectady, New York, and** ***J. E. Burke,*** **Knolls Atomic Power Laboratory. John Wiley & Sons, Inc., New York, 1953. xi + 340 pp. Many figs. Tables. 15 × 23.5 cm. $7.**

IN RECENT years so many research chemists, physicists, and engineers have been performing experiments in metallurgy that a need has arisen for a laboratory handbook that will describe elementary techniques in metallurgy other than metallography. This book presents an unusual approach in that the most basic details are presented, leaving nothing to the imagination.

The twelve chapters are entitled Methods of Obtaining High Temperatures, Measurement of High Temperatures, Control of Temperature, Refractories, Controlled Atmospheres, Vacuum Systems, Melting and Casting, Heat-treating Techniques, Fabrication of Metals, Powder Metallurgy, Preparation of Pure Metals, and Preparation of Metal Single Crystals. At the end of each chapter there is a list of references to authoritative books and commercial companies in that particular field. For instance, the excellent chapter on vacuum systems has sections which include pumps, traps, measuring devices, seals, valves, system design, and leak hunting, as well as references to Dushman and to Guthrie and

Wakerling, among others. The other chapters are similarly organized. Commercial sources of material and equipment are found throughout and many hours of searching commercial literature will be saved by the tables which present properties and suppliers for ceramic and refractory materials and for pure metals.

Some researchers will claim that the authors' approach is too naïve in many instances. This may be true to some extent, although many of the techniques which are described are usually not discovered until some years have been spent in the field. The book is not applicable as a text, but will be found to be extremely useful to graduate students and to scientists in research and development laboratories.

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● COPPER

Edited by *Allison Butts*, Head, Department of Metallurgical Engineering, Lehigh University, Bethlehem, Pennsylvania. American Chemical Society Monograph Series No. 122. Reinhold Publishing Corp., New York, 1954. xii + 936 pp. Illustrated. 16 × 23.5 cm. $20.

A MONOGRAPH of this type, being so comprehensive and having so many authors, cannot be adequately evaluated in the space afforded a book review. A glance at its contents is sufficient to verify the claim of the publisher that it is "the most complete, up-to-date treatise on copper ever published." According to the preface, each chapter has been written by its author(s) "in his own way, without attempting to meet any prescribed outline or arrangement." It was the intent of the editor "to avoid inadvertent omissions of important topics and to prevent in so far as possible needless duplication." For the most part, these aims have been achieved.

One surprising omission has nevertheless apparently occurred. There seems to be no mention of the important development of vacuum melting and casting of copper. This was reported by National Research Corporation at the Cambridge High Vacuum Symposium of the A. C. S. Division of Industrial and Engineering Chemistry, October, 1947, and was published in 1948. This company has been producing it for a number of years in steadily increasing amounts. Tonnagewise, vacuum-melted copper may be only a small part of the 750 thousand tons of copper produced in the United States each year, and from the standpoint of volume, failure to mention it might be excused. Chemists, however, are interested in properties of pure elements; this vacuum-produced commercial grade of copper has higher density and better mechanical properties, and the electrical conductivity of as-cast ingots is over 100 per cent of that of the international annealed copper standard, based upon OFHC copper. Among other advantages, vacuum-produced copper has contributed longer life to evacuated electronic tubes because of its superior outgassing characteristics.

To viewers of copper roofs, the omission of the word "patina" from the index is surprising. The word appears in the book in several places (*e. g.*, on pages 3, 392, and 804). The correct composition (basic copper sulfate or chloride) is given on page 392 in an excellent chapter on corrosion of copper, but on page 804, in a section called "simpler inorganic compounds of copper," the traditional, but incorrect, designation as basic copper carbonate as retained. The subject index is far from adequate for such a treatise of over 900 pages and seriously reduces its usefulness as a reference. To cite a few more examples, words like "verdigris," "blue vitriol," "Scheele's green," and "copper phthalocyanine" are omitted, although mentioned in the text, while "copper naphthenate," "phenyl copper," and "Paris green" are cited. It is difficult to determine what criteria were used in compiling this index. The name index, on the other hand, is very complete; it includes names of all authors and co-authors of papers referred to in the various chapters.

Conservationists will be interested in the first chapter, in which the alarmingly rapid depletion of copper deposits is mentioned—"complete exhaustion in about 45 years." The possibility of substituting aluminum for copper is thoroughly surveyed. It is claimed that aluminum would enter more largely into industrial wiring if it could be as easily soldered as copper. For such purposes the rule of thumb is "one pound of aluminum is roughly the equivalent of two of copper" (page 18).

The reviewer read with interest about copper-clad stainless steel but could not find out how the currently popular cooking utensils are made, nor what mixtures of compounds are used to keep the copper bottoms bright. The copper-clad seal-in wires used in electric light bulbs are not mentioned in spite of their pervasiveness in modern civilization. To summarize, one gets the impression in scanning this book that the winning of copper and the large tonnage production of copper products are very competently covered, but that many of the little items a teacher might like to look up are not there, or, because of the inadequate index, are very hard to find. It is obvious that this is a book that should be added to every technical library, but not being truly encyclopedic, it cannot be expected to yield answers to every question about copper that students might think up.

LAURENCE S. FOSTER

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● INDUSTRIAL STOICHIOMETRY

Warren K. Lewis, Arthur H. Radasch, and _H. Clay Lewis,_ Professors of Chemical Engineering at, respectively, Massachusetts Institute of Technology, Cooper Union School of Engineering, and Georgia Institute of Technology. Second edition. McGraw-Hill Book Co., Inc., New York, 1954. ix + 429 pp. 16 × 24 cm. $7.50.

TEXTBOOKS in chemical engineering essentially started with Walker, Lewis, and McAdam's "Principles of Chemical Engineering" in 1923. The first chapter in this text was on industrial stoichiometry, the importance of which became so apparent that in 1926 a book of this title was published with W. K. Lewis and Radasch as authors. It was the second important text in chemical engineering. It has remained unchanged since 1926 until the appearance of the completely rewritten second edition, in which H. C. Lewis has joined as co-author.

The changes in the new edition have been numerous, and considerable expansion has occurred from the 174 pages of the first edition to the 429 pages of the second. There also has been an expansion in the viewpoint, for now the authors consider not only material and heat balances, as they did previously, but also equilibrium relationships and the rate at which the change occurs.

The introduction still attempts to give the student all of the tools necessary for problem working. In addition to describing the ideal gas laws in one paragraph, another has been added on nonideal gases, and now gas law calculations are reduced to substitution into a formula, rather than the thoughtful application of Charles' and Boyle's laws and the z-factor. Heat capacities and enthalpy are discussed in two paragraphs, accompanied by two figures giving heat capacities from 0 to 6000°F. How accurately can these be used to give values for a heat balance over a boiler furnace? Also missing from the introduction is the vigorous expression that made W. K. Lewis famous as a teacher. Formerly the student was told: "Changing bases in the midst of a computation is shifting gears with the clutch in and the throttle open." Now he is informed: "A change in basis should be scrupulously avoided in the middle of any specific computational operation." One of the authors must have been writing government instruction sheets!

The former chapter on Fuels and Combustion has been expanded to chapters on Gaseous and Liquid Fuels, Energy Balances and Equilibrium, and Solid Fuels. Much new and worthwhile material is given in the discussion of energy balances and equilibrium. The other two chapters give much on combustion calculations that was given before. An innovation is the flow-

sheet or sketch that precedes the selection of the basis and which is to assist the student in visualizing the process. The reviewer objects violently to the type of equation on page 44 using an unknown to represent moles of water vapor in air. It is confused thinking; the authors have not made clear that from Dalton's law they should show that the ratio of partial pressures is also the ratio of moles, for ideal gases.

The previous chapter on Gas Producers now is entitled Secondary Fuels. Sulfur Compounds, Lime and Cement, Metallurgy, and Design Problems have been expanded considerably. New chapters have been added on Nitrogen Compounds, Fixed Alkalis, and Ceramics. Many new applications of stoichiometric methods are given both in illustrated problems and in student exercises.

When is the M. I. T. group going to stop using the archaic *mol*? A look in the dictionary, or a letter to the A. C. S. Committee on Nomenclature, Pronunciations and Spelling, would inform them that *mole* is correct.

The new edition is bigger, covers more industries, has more problems, and costs three times as much as its predecessor. But it is doubtful that the new edition will regain the position once held by the old edition. With its new industries and new examples the book will probably become an adjunct to courses in industrial chemistry where technology and stoichiometry will be taught together. It probably won't be the introduction to chemical engineering that students had for so many years. Unfortunately, "bigger and more coverage" doesn't mean a more lucid presentation of the fundamentals that a sophomore can grasp and apply.

KENNETH A. KOBE

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● THE BIOCHEMISTRY OF GENETICS

J. B. S. Haldane, F.R.S. The Macmillan Company, New York, 1954. 144 pp. 7 figs. 22 × 14 cm. $2.75.

GENETICS is both the most interesting and the most unifying of the biological sciences. It brings together in one general account the diverse phenomena of heredity, evolution, and biochemistry. It is therefore appropriate that chemists be informed from time to time of progress in this field, especially where it touches on biochemistry. The present book is based on lectures given by J. B. S. Haldane at the University College, London. It is not a textbook, but is rather a series of interpretative reviews of various topics in the field of biochemical genetics intended primarily for biochemists. The author attempts to answer four questions: What do genes do? How do genes do what they do? What are genes biochemically? How are genes reproduced and how is their process of reproduction sometimes altered so as to give a gene of a new type?

Chapter I deals with the elements of genetics. It is no easier to explain the elements of genetics in ten pages than it would be to explain the elements of chemistry in the same space, and despite the fact that these pages are written by a master of the art of the scientific essay, it will be a perceptive biochemist indeed who derives much understanding of genetic principles from them. Most biochemists will never emerge from the first paragraph.

Chapter II briefly takes up some topics relating to the genetics of blood. The question mainly considered is whether the blood cell antigens, the globin part of hemoglobin, and certain plasma proteins may be considered as primary products of gene action. The answer is that available evidence suggests that they may be primary products in some cases, but that it is too early to be sure.

In Chapter III, entitled Genes Controlling Synthesis in Fungi, we come to one of the main themes of the book, namely, the genetic control of metabolic pathways. This chapter deals chiefly with the biochemical genetics of *Neurospora*, although examples are given from *Aspergillus* and other fungi. Haldane shows a wide familiarity with the extensive literature of this subject. Again, however, the intention is not to present a systematic or inclusive treatment of the field, but only to discuss some of the principles involved. The chapter is already out of date, especially in regard to enzymatic studies on mutants, but this does not seriously affect the interpretations given, except in the confusing isoleucine-valine case, the interpretation of which has been considerably simplified by recent enzymatic evidence from *Neurospora* and *E. coli*. In the discussion of the nicotinic acid series of mutants, an error is made in stating that quinolinic acid is not utilized by *Neurospora* mutants. A few other points made by Haldane are debatable. For instance, it is probably not true that serine is produced in the cleavage of cystathionine to homocysteine; and it is has not been shown that sulfite and alanine combine to form cysteic acid biologically, although the reverse reaction is known.

Chapter IV deals with the biochemical genetics of yeasts, bacteria, and viruses. The treatment here can best be described as perfunctory. It is evident that the author is much more interested in sexual organisms with clear chromosomal genetics than in microorganisms of dubious genetic status. Much work on the biochemistry of bacterial mutants is passed over, not to mention studies such as those of Granick on the biosynthesis of chlorophyll in mutants of the asexual alga, *Chlorella*.

Chapter V considers the higher plants and Chapter VI the higher animals, including man. These are fields in which Haldane has made personal contributions, and the treatment is much more lively, particularly in Chapter VI, which the reviewer found especially rewarding. The pathway by which tyrosine is converted to homogentisic acid is no longer considered to go through 2,5-dihydroxyphenylalanine, as shown in Figure 6, however, but through *p*-hydroxyphenylpyruvic acid to 2,5-dihydroxyphenylpyruvic acid.

Chapter VII briefly reviews recent examples of non-Mendelian inheritance in yeasts, Protozoa, and mammals. The greater portion of the chapter, however, is devoted to an attack on the views of Lysenko and his British scientific counterpart, Hinshelwood. Haldane concludes: "A student of higher plants and animals, therefore, finds no reason to agree with Kilkenny and Hinshelwood's conclusion that 'the rigidly localized gene is likely to be a limiting case and the purely Mendelian type of segregation to be rather rare,' or with the more dogmatic and more minatory pronouncements of Lysenko to the same effect." He is opposed to dogmatic assertions as to the nonexistence of all Lamarckian effects, however, and is willing to concede that something of this sort may occur in bacteria. He finds that a dogmatic attitude has been adopted by some workers, "particularly in America." In other matters, too, Haldane has found reason to criticize the attitude of American geneticists, although he clearly admires their accomplishments.

Chapter VIII deals with the nature of mutations and the chemical structure of the gene. Haldane summarizes the present status of the work on the chemical induction of mutations, but one can doubt his conclusion that this work proves that most of the genetic effect of radiations is due to the production of mutagenic substances within the nucleus, rather than to direct hits on the chromosomes. In citing the proof by Stone, Wyss, and Haas that ultraviolet irradiation of the medium produces substances which are mutagenic for bacteria, Haldane fails to mention that this effect was obtained only with wave lengths shorter than 2000 Å.—wave lengths which cause the photochemical decomposition of water. On the other hand, it was shown long ago by Stadler and Uber that wave lengths in the neighborhood of 2600 Å. are mutagenic in experiments in which cells are irradiated directly and that their effectiveness parallels the ultraviolet absorption curve of nucleic acid. It seems clear that with respect to ultraviolet, direct effects predominate at long wave lengths and indirect effects at the shorter wave lengths. With regard to the chemical nature of the gene and of gene reproduction, Haldane's discussion is unfortunately dated by the fact that it was written before the publication of Watson and Crick's paper on the structure of desoxyribonucleic acid. Nevertheless, it contains material which will be of interest to biochemists approaching this subject for the first time.

The final chapter, entitled Tentative Conclusions, contains an

informal discussion of a variety of topics of current interest in biochemical genetics—*e.g.*, position pseudoallelism, the possible origin of the vitamins as direct gene products, and biochemical evolution. Haldane returns to develop a point made earlier—namely, that "The genes may ... be regarded as intracellular organs.... That is to say, the conceptions, and to some extent the technique, of large-scale physiology may be applied to them. We can, of course, also regard them from a more biochemical point of view, as catalysts with many of the properties of ordinary enzymes." Although the reviewer would not deny the possibility that some useful insights may be obtained by regarding the genes as intracellular organs or as ordinary enzymes, it seems that in doing so one is in danger of losing sight of the main point of genetics—that is, its quasi-atomic nature, to use Haldane's phrase. The genes are individual molecules, present in a concentration of only one or two per cell. Their behavior is not describable by the statistical laws of physiology or chemistry, but by the laws of single particles. It is an important fact that the cell is a chemical system in which large changes in reaction rates can be induced by the alteration or destruction of a single gene—*i. e.*, a single molecule. The study of genetics thus shows that the cell is unlike any ordinary chemical system, and this, for the chemist, is one of the most fascinating aspects of genetics.

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• SPOT TESTS. VOLUME I: INORGANIC APPLICATIONS. VOLUME II: ORGANIC APPLICATIONS

***Fritz Feigl,* Professor, the University of Brazil. Translated by *Ralph E. Oesper.* Fourth English edition. Elsevier Publishing Company, Houston, Texas, 1954. Volume I: xii + 518 pp. 37 figs. 8 tables. $6.50. Volume II: xv + 436 pp. 32 figs. 37 tables. $6.25. 15.5 × 23.5 cm.**

This two-volume treatise on spot tests originally appeared in 1931 as one volume. Since then it has grown extensively in size, and the fourth English edition has now been published as two separate manuals, one on inorganic applications and the other on organic applications, each complete in itself and presenting an extensive, critical, and up-to-date survey of procedure and application of spot tests to both research and routine work. An important feature of the fourth edition is the wealth of new material, including many new tests developed by the author and his collaborators, most of which are described for the first time in these volumes. The arrangement of the material and the description of tests is the same as in previous editions, except for typographical changes to save space, and omission of the bibliography of papers dealing with technical applications of spot testing.

"Spot Tests" is a companion text to the author's book on the "Chemistry of Specific, Selective and Sensitive Reactions" published in 1949, in which is assembled and arranged the critically selected material that is related to the specificity, selectivity, and sensitivity of analytical procedures.

In Volume I "tests which have been thoroughly tested by the author have been described in detail." These were selected not only from the standpoint of practical usefulness but also to possibilities of improvement and to important details in the chemical basis of the particular test. The descriptions of the tests have been made so that they may easily be translated into the macro scale, and also applied to inorganic chromatography, though no effort was made to include the latter technique, since excellent texts in this new and rapidly growing field are available. The introductory chapter, Development, Present State and Prospects of Inorganic Spot Tests Analysis, has been completely rewritten in cooperation with Philip W. West (Louisiana State University); the latter also contributed Chapter II, Spot Test Technique.

Volume II is an outgrowth of the previous edition of "Spot Tests, Inorganic and Organic Applications," which included slightly over 120 pages devoted to organic spot test analysis. It now becomes an independent manual. In order to make it truly a self-contained monograph, the chapter on Spot Test Technique in Volume I has been included in Volume II. "Furthermore, all tests for inorganic materials which are left in the residue after organic samples are decomposed, have been described in sufficient detail, so that reference to Volume I in such cases will not be necessary, except for amplification of background information." The author emphasizes, however, that this monograph is not intended to replace the well tested manuals dealing with qualitative organic analysis but merely to supplement such works.

The chapter on preliminary tests has been entirely rewritten and many new tests for functional groups and individual compounds have been added. The book contains the complete or orienting description of more than 200 tests. The underlying chemical reactions have been stressed when possible, many structural formulas are given, and the pertinent data regarding sensitivity and reliability have been included for most of the tests.

Both volumes list many references (about 1500) to the original literature; these will be found at the end of each chapter. The last chapter in each volume consists of a tabular summary of the limits of identification attained by spot tests (Volume I, cations, anions, and several free elements; Volume II, certain elements that are most frequently present in organic compounds, characteristic groups, and many individual compounds). Each volume is well indexed (both author and subject).

R. E. Oesper, well known translator of Feigl's books, is to be congratulated for making "Spot Tests" available in clear and concise English. Printing and paper are good and the books have attractive flexible cloth bindings.

"Spot Tests" will be a useful source of information not only to analytical chemists but also to organic chemists, pharmaceutical chemists, and biologists, as well as to advanced chemical students. Research workers in analytical chemistry will find these volumes stimulating and helpful.

JOHN H. YOE

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• ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. VOLUME XII: SABADINE TO STILBESTROL

Edited by *Raymond E. Kirk* and *Donald F. Othmer,* Professors and Heads, Departments of Chemistry and Chemical Engineering, respectively, Polytechnic Institute of Brooklyn. Assistant editors, *Janet D. Scott* and *Anthony Standen.* The Interscience Encyclopedia, Inc., New York, 1954. xvi + 955 pp. 19 × 27 cm. Single copy price, $30. Subscription price, $25.

The inorganic chemist and industrial chemist are the large winners in Volume XII of E.C.T., which runs mainly to subjects in these two fields. Selenium, silicon, silver, and sodium are the elements appearing in this volume, along with a discussion of alloys and compounds, including special sections on salt (sodium chloride) and salts in general. Silica and its ramifications cover considerable space, with silicate minerals, synthetic insoluble silicates, soluble silicates, vitreous silica, and silica gel. Of theoretical interest is the section on the stereochemistry of inorganic compounds.

The analytical chemist will be interested in the section on sampling. The organic chemist will turn to the large section on the stereochemistry of organic compounds. The sections on saponins and sapogenins, sterols and steroids, starch, serums, and serology will interest both the biochemist and organic chemist.

The chemical engineer finds a number of unit operations discussed: sedimentation, size reduction, and size separation. Other useful topics are size measurement of particles, solvent recovery, sprays, and steam.

Industries discussed include steel, soap, salad dressing, shortenings, shale oil, silk, silicones, soybeans, and sewage treatment.

Extensive tables and charts for industrial solvents give properties of value to the industrial user and research worker.

If your garden doesn't grow, read the section on soil chemistry. If your dissimilar metals won't join together, read about solders and brazing alloys. Need a mirror? Read about silvering (and other types of mirror surfaces). Bothered by smog? Read about smokes and fumes, and the control measures. Does dandruff make you unpopular? The interesting and authoritative section on shampoos and other hair preparations will tell you what is best for you.

The billboards say that safety is everybody's business. This volume actually starts with a 36-page discussion of safety, organization, reports, hazards, and finally sources of information on safety.

Volume XII is an excellent one that brings us almost one letter closer to the approaching end of the alphabet.

KENNETH A. KOBE

University of Texas
Austin, Texas

● ELEMENTARY FLUID MECHANICS

John K. Vennard, Professor of Fluid Mechanics, Stanford University. Third edition. John Wiley & Sons, Inc., New York, 1954. xii + 401 pp. 214 figs. 14 × 22 cm. $5.50.

This text is an introduction to fluid mechanics intended for third-year engineering undergraduates. Emphasis is placed on analytical development of formulas for engineering applications of fluid motion, but the analysis is carried out with a minimum of mathematical and physical complexity. The author's intention to make the book self-explanatory to the student, thus freeing the instructor for more advanced subjects, appears to be successful.

The text commences with introductory material on the physical characteristics of fluids and hydrostatics; then continues with four chapters on frictionless fluid flow, both incompressible and compressible. As compared with the previous edition, the present one has a simplified discussion of streamlines and the energy equation obtained by confining the analysis to one-dimensional flow. The remaining chapters describe the flow of a real fluid through pipes and channels and around immersed objects. Dimensional analysis and fluid measurements each have one chapter. New material added to the present edition includes discussions of compressible fluids in pipe flow, and lift and drag of airfoils in compressible fluids.

CHARLES COX

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● GREAT DISCOVERIES BY YOUNG CHEMISTS

James Kendall, Professor of Chemistry in the University of Edinburgh, President of the Royal Society of Edinburgh. Thomas Nelson & Sons Ltd., London, 1953. xii + 231 pp. 34 plates. 14 × 20.5 cm. 12/6 net.

This book has a thesis to prove, namely, that there are "very few significant discoveries in chemistry not due to juveniles." The reader easily confirms this statement. And if he has any doubt, as the author states, "let him attempt to outline the contents of a volume entitled 'Old Chemists and Great Discoveries,' taking a very liberal point of view with regard to the first adjective. If 'old' means over seventy, or even over sixty, the book would be practically all cover; if over fifty-five, it would still be very slim. Reduction of old age to fifty would help somewhat, but the available material would still be rather scrappy and second-rate. Not only have young men and women made most discoveries in chemistry, but those discoveries have been the greatest."

The volume has been written so clearly and simply and with such informal approach that it cannot help but appeal to the general reader whether he be young or old, interested in science or not. As the chapter headings indicate, the book contains more than biographical sketches. One learns how scientists work, their attitude toward their work, how the masters taught, and the close association of master and student. Faraday's "Chemistry of a Candle," pp. 64–8, is an example of many valuable source materials.

The interesting account of the "Quest of Couper" is a fine illustration of the "brotherhood of science" in trying to do justice to a lost genius many years after his death. In the ninth chapter an understanding and appreciative account of the young American chemists is included. James Woodhouse, the founder, in 1792, of the Chemical Society of Philadelphia (long considered the oldest chemical society in the world), and Robert Hare, who invented an electric furnace, are not so well known as Charles Hall and Irving Langmuir. There is a personal and intimate touch in the account of the contribution of the latter, for Dr. Kendall claims him as his friend of forty years. His last-told hero in science is the young prince Albert Edward (afterward King Edward VII) who offers inspiration from high places.

The 32 plates enhance the value of the book. Most of them are portraits of the heroes in their youth.

SISTER M. CONSILIA HANNAN

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● TITANIUM AND ITS COMPOUNDS

Gordon Skinner, Herrick L. Johnston, and *Charles Beckett.* Herrick L. Johnston Enterprises, Columbus, Ohio, 1954. iii + 174 pp. 27.5 × 18 cm. Cloth, $5. Paper, $3.50.

This book began as a literature survey at the Ohio Cryogenic Laboratory and became a very useful collection of data that will be of help to chemists and metallurgists who are interested in titanium. Its major contribution is the collection in one place of tables of thermal functions of a selected group of titanium compounds, namely, the hydrides, oxides, halides, nitrides, carbides, and alkaline earth titanates and information concerning their production and reactions. There is a selected bibliography of 553 references to the relevant literature up through 1951.

LAURENCE S. FOSTER

Belmont, Massachusetts

● THE BIOCHEMISTRY OF THE NUCLEIC ACIDS

J. N. Davidson, Gardiner Professor of Physiological Chemistry, University of Glasgow. Second edition. John Wiley & Sons, Inc., New York, 1954. viii + 200 pp. 22 figs. 4 plates. 11 × 17 cm. $2.25.

This edition contains much of the material presented in the original work published in 1950. Some material formerly presented and now obsolete has been omitted and much new information has been added. This is included in the chapters on the hydrolysis products of the nucleic acids, the structure of the polynucleotides, the cell nucleus, and the biosynthesis of the nucleic acids.

This book makes no claims to being a monograph on the subject. The author points out that it is intended as an elementary outline; however, despite a keen eye on economy of paper and print he has given a highly readable account of this rapidly expanding field.

The excellent bibliography included at the end of each chapter makes the work valuable to both the general reader and the researcher in biochemistry.

LIONEL JOSEPH

San Diego State College
San Diego, California

● ADVANCED ORGANIC CHEMISTRY

E. Earl Royals, **Associate Professor of Chemistry, Emory University. Prentice-Hall, Inc., New York, 1954. xii + 948 pp. 23.5 × 15.5 cm. $10.**

IN RECENT years second courses in organic chemistry, whether on the undergraduate or beginning graduate level, have commonly become courses on electronic theory and organic reaction mechanisms. This trend is of recent enough origin that relatively few suitable texts are at present available, in unhappy contrast to the plethora of those on the elementary organic level. The appearance of a book as comprehensive and as lucidly, often vividly, written as the present "Advanced Organic Chemistry" is thus a welcome event. In 846 pages of actual text Dr. Royals has presented a wealth of factual material interwoven with unifying theory. He has pointed out that in addition to its use as a textbook the book "is intended [to be] useful to graduate students throughout their graduate training, [and that] it is also hoped that practicing organic chemists desirous of maintaining contact with the broad field of organic chemistry and the more modern development therein will find it useful."

Although the claim on the dust cover that "no experimental fact is quoted without complete documentation" is somewhat exaggerated, the book is generously documented with more than 1500 literature references, approximately 35 of which carry the literature to 1950–51. The author index and thorough subject index comprise a total of 102 pages.

In the first chapter, entitled The Structure and Reactivity of Organic Compounds, the author presents the fundamentals of electronic theory as applied to the resting and reacting molecule and general principles of chemical kinetics and equilibrium which are to be used throughout the later discussions. Electronic theory is presented as an "aid to the understanding and memory, not as a predictive tool." This first chapter is a composite of material to be found in Pauling's "Nature of the Chemical Bond," Wheland's "Theory of Resonance," Remick's "Electronic Interpretations of Organic Chemistry," Ingold's *Chemical Review* article (and recent book, although the latter appeared too late to be used directly), Hammett's "Physical Organic Chemistry," and Eyring's treatments of rate processes. It represents a well organized and pedagogically useful survey of current ideas and lays the groundwork for the blending of facts and theory throughout the remaining chapters.

In logical sequence the author then develops in successive chapters the chemistry of the alkanes, the cycloalkanes, the alkene linkage, aromatic hydrocarbons, and the alkynes, and finally devotes four chapters to carbonyl compounds. Making use of the following general scheme: (first) methods of synthesis, and (second) chemical behavior, the chemistry of the hydrocarbons and their most important univalent derivatives is systematically evolved. For example, the chapter on the alkene linkage begins with a survey of aliphatic halides leading into studies of the mechanisms of aliphatic substitution and elimination reactions in general and then logically merging into the syntheses of the alkenes through elimination reactions. The discussion of chemical behavior follows this pattern: isomerization, free radical and polar polymerizations, oxidations, addition of halogen (the discussion of the mechanism of which allows a smooth transition to a general discussion of neighboring group participation in displacement reactions), and this is followed by additions of unsymmetrical reagents to the alkene linkage, and so on. In the four chapters on carbonyl compounds all classes of carbonyl compounds—aldehydes, ketones, acids, esters, amides, etc.—are considered concurrently. The material is introduced with a consideration of the nature of the carbonyl group, and the remaining three chapters are devoted, respectively, to methods of preparation of carbonyl compounds, addition reactions of the carbonyl group, and reactions dependent upon active hydrogen.

There are a surprising number of typographical errors in formulas, which may be disturbing to students. Although the author has made a serious attempt to document adequately throughout, he has occasionally been neglectful, as for instance in his discussion of dehydrations of the Tschugaev type, where he presents without acknowledgment a cyclic mechanism like that proposed in 1938 by Hurd and Blunck, in 1940 by Hückel, Tappe, and Legutke, and in 1941 by Stevens and Richmond and discussed in Alexander's "Ionic Reaction Mechanisms." It is no fault of the author if a book with the broad coverage of the present one is in places incomplete by the time it reaches the publication stage. Foreseeing this inevitability, he has indicated that he "endeavored to so present mechanistic considerations that future research will require that what is here given be extended and elaborated rather than discarded." Nevertheless, some readers may feel that the book has suffered from the omission of pertinent contributions and concepts available at what appears to be the "cut-off" date (1950–51). The reviewer would cite contributions to the field of aromatic substitution—particularly those by the English school—applications of molecular orbital theory to organic chemistry, and recent contributions to the stereochemistry of ring compounds and to the field of nucleophilic substitution reactions as perhaps outstanding omissions of this type.

However, no one textbook could ever satisfy all readers, and Dr. Royals has skillfully developed here a stimulating picture of basic organic chemistry, neither sacrificing factual material nor neglecting theory, as so often is the case in comprehensive treatments of fact. The book is a rich source of descriptive material set in a framework of mechanistic rationalization.

FRANCES BERLINER

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● FENTON'S NOTES ON QUALITATIVE ANALYSIS

B. C. Saunders, **Fellow and Charles Kingsley Lecturer in Natural Sciences, Magdalene College, Cambridge University, England. Revised edition. Cambridge University Press, New York, 1953. 124 pp. 9 figs. Many tables. 19.5 × 25.5 cm. $2.75.**

AS INDICATED by the title, this book presents a summary of qualitative analysis (practical). The form and content of the book is reminiscent of a lecturer's set of notes used in outlining the essential chemistry to be considered in a thorough laboratory course in qualitative analysis.

Part I summarizes the principal reactions of common cations and anions. Part II presents outlines of analytical procedure including both dry and wet tests. Analysis in the dry way includes observation of the color of salts, closed tube ignitions, blowpipe operations, flame tests, and bead tests. Analysis in the wet way is presented in the classical manner based on a chloride group, acidic sulfide group, hydroxide (NH_4OH + NH_4Cl) group, basic sulfide group, and a carbonate group separation of cations. Magnesium is separated as the phosphate and standard tests are used to identify the soluble group. Various classification tests are presented for acid radicals and for gases. A number of alternate procedures are suggested and discussions of the fundamental reactions are included.

Part III is a "modernization" of qualitative techniques. Some semimicro methods are outlined and spot test and chromatographic techniques are discussed briefly.

The book is remarkably free from errors and is well printed and bound. The presentation would seem to make the book best suited for an informal class or for reference for serious students wishing to extend their knowledge of ionic reactions and qualitative chemistry.

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Out of the Editor's Basket

Portable Refrigerator Unit

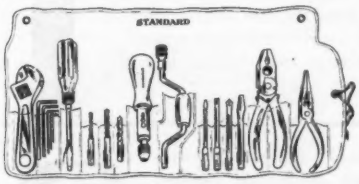
A portable refrigerator unit, complete with thermostat, mobile cooling coil weighing only 45 pounds, and which plugs into any 155 volt a.-c. outlet, is marketed by A. Daigger & Co., 159 W. Kinzie St., Chicago 10, Illinois.

This unit can be put on the job instantly, since it involves no installation difficulties. The portable thermostat is merely set for the desired temperature, cooling coil placed where desired, and current switched on. There are no pipe connections or adjustments to make, no mechanical work to be done.

Models are available with or without cabinets, in several sizes, also with auxiliary equipment such as a force-flow circulating pump and heat exchanger for handling liquid coolants.

Tool Kit for the Laboratory

The wide use of instruments and apparatus in the laboratory often necessitates the servicing or the replacement of parts.



This requires the use of tools such as screw drivers, allen wrenches, pliers, brace and bit, and other essential items. To meet the need for use of tools in boring a hole, wiring a simple job, tightening a screw, or loosening a bolt in the average laboratory, Standard Scientific Supply Corp., 34 W. 4th St., New York 12, New York is now offering a new complete kit of tools. The set contains 19 units which can be interchanged to make many combinations of tools. The kit is supplied in a strong vinyl case which folds up to 9×4″ and can fit into a corner of a desk drawer.

Large Capacity Blendor

A new Waring Blendor of one gallon capacity, designed for high speed blending, pulping, and mixing in larger quantities than handled by previous models is announced by Central Scientific Co., 1700 Irving Park Rd., Chicago, Illinois.

It has five speeds and is operated with push button controls. Speeds range from 8000 r. p. m.'s to 16,000 r. p. m.'s. The unit functions on alternating current of 115 volts with a $1^1/_2$-h.-p. motor, and is the first high-speed blending device of this kind capable of holding more than 37 ounces. The base of the unit can be fastened permanently to a working surface, and the stainless steel receptacle can be lifted off for emptying and cleaning.

Combination Hot Plate and Magnetic Stirrer

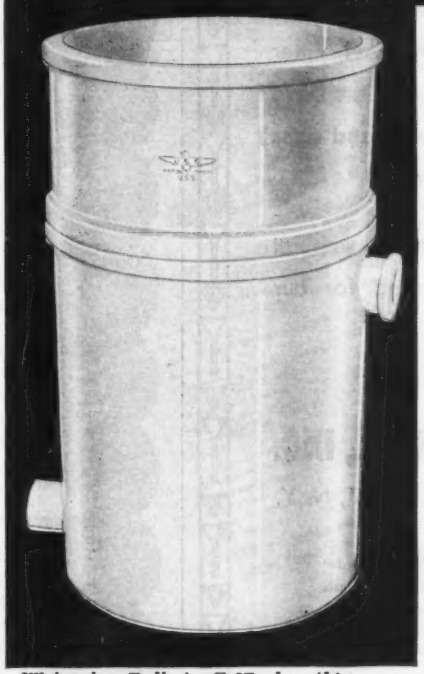
A hot plate-magnetic stirrer which makes it possible to heat liquids while stirring magnetically is a new product of the Arthur S. LaPine & Co., 6001 S. Knox Ave., Chicago 29, Illinois. The base of the apparatus is a light casting that houses the controls for heating and stirring and the stirrer motor. The hot plate assembly plugs into the top of the base and is removable. A stainless steel support rod threads into the base. A glass-enclosed stirring magnet is supplied.

Rheostat control of the motor enables "dialing in" the most effective speed for stirring a particular liquid. An input controller obtains infinitely variable heating from 0 to 400 watts. Both rheostat and input controller have off positions, so that stirring and heating are independent of each other and can be used separately or together. Motor and magnet are fan cooled for long life, and the plug is grounded for safety.

New Product for Kjeldahl Determinations

Test chemicals for Kjeldahl nitrogen determinations are now available in new packaged form, mixed in precise proportions and ready to drop into the test flask. The new product, Kel-Pak Powders, is

in gleaming white porcelain



One of the most popular of U. S. Stoneware's line of Ceramic Vacuum Filters is this two-piece porcelain unit designed specifically for laboratory and pilot plant use.

Available in two sizes (top capacity 1 gallon or 2½ gallons), Figure 2070 B Filter is light enough to be easily portable, yet strong enough to withstand a complete vacuum. The perforated filter support plate is an integral part of the upper unit. The finish is as smooth and easily cleaned as a china dish. And being white chemical porcelain, the filter will handle all chemicals except hydrofluoric acid, and hot caustics.

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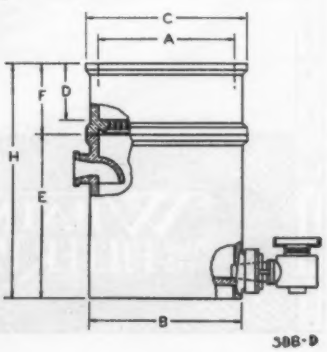

Size	Dimensions, Inches A	B	C	D	E	F	H	Faucet Size	Capacity Gals. Top	Capacity Gals. Bottom	Weight Lbs. Top	Weight Lbs. Bottom
A	10	11	11½	4	12	5	17	½	1	2	10½	19½
B	12	13¼	13¾	6½	16¼	7¼	23½	½	2½	5	20½	28½

308-D

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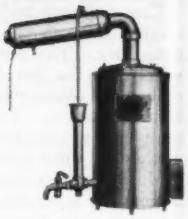

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produced by Laboratory Reagents, Inc., 3030 Main St., Kansas City, Missouri. The formulas for the powders conform to A.O.A.C. standard methods.

The chemicals used to make the powders are precision weighed, thoroughly blended, and carefully ground in large quantities. Every batch is analyzed for uniformity. Kel-Pak powders are available in three standard formulas for determinations by the Kjeldahl Method, the Gunning Method, or the Kjeldahl-Wilfarth-Gunning method. Samples and complete information are available from the manufacturer.

Vacuum Stirrer

Labline, Inc., 217–221 N. Desplaines St., Chicago 6, Illinois, announces their new Stir-O-Vac for stirring under vacuum without mercury seal. The unit is supplied with a high speed $^1/_6$-h.-p. series motor for operation up to 20,000 r.p.m. Motor comes complete with special chuck and 3 prong clamp for clamping to support rod. Can also be furnished less Cruciform impeller and shaft for user to supply his own special stirrer blades to suit any particular test. Labline has a bulletin No. 1280 A available on this.

New Centrifuge

The new Model U is the latest addition to International Equipment Company's complete line of laboratory Centrifuges. The modern cabinet design matches standard laboratory furniture units and the stainless steel auxiliary top provides extra bench space when the Centrifuge is idle.

New features, not heretofore available in a laboratory Centrifuge include a new stainless steel guard bowl interior, a built-in electric tachometer, an electric time clock, an aerodynamic guard bowl ventilating system with dual air filters, a new vibration dampening system, and 84 interchangeable accessory combinations for every laboratory purpose.

Bulletin J-1954, containing complete details, may be obtained by writing to the International Equipment Co., Dept. F., 1284 Soldiers Field Rd., Boston 35, Massachusetts.

Improved Vacuum Oven

Precision Scientific Co., 3737 W. Cortland St., Chicago, Illinois, has redesigned its Thelco Vacuum Oven for greater accuracy and durability. Ribbon-type heater elements are used. A sensitive hydraulic thermostat with external adjustment knob permits exact resetting to temperature. The insulated working chamber is made of cast aluminum. A stainless steel drip pan is supplied, as well as a new formula neoprene rubber gasket. The door is hinged at the top for easier closing and use of less space. Catalogue 331A covering this item is available.

Bibliography on Titanium

The following bibliography on titanium was compiled by L. S. Foster, Belmont, Massachusetts.

Pamphlets

"Titanium," Pigments Dept., E. I. du Pont de Nemours and Co., Wilmington, Delaware. (Has a good bibliography.)

"Properties of Titanium and Titanium Alloys," Mallory-Sharon Titanium Corporation, Miles, Ohio.

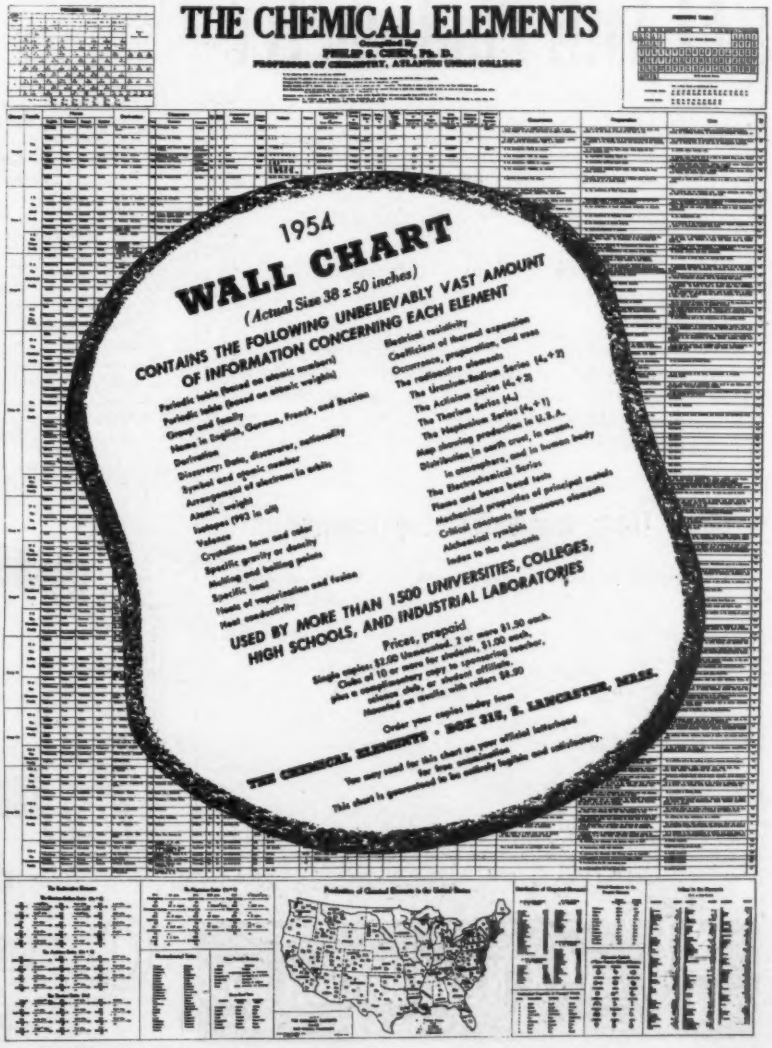
Rem-Cru Titanium Review, published quarterly by Rem-Cru Titanium, Inc., Midland, Pennsylvania. (Volume 1, no. 1 is dated June, 1952.)

"Handbook on Titanium Metal," Titanium Metals Corporation of America, 60 E. 42nd St., New York 17, New York.

"Manual 82, Titanium and Its Alloys," *Materials and Methods Magazine*, Reinhold Publishing Corporation, 430 Park Ave., New York 22, New York.

Books

"Titanium and Titanium Alloys," by John L. Everhart, Reinhold Publishing Corp., 430 Park Ave., New York 22, New York. A Reinhold Pilot Book, published in 1954. It is a pocket-size, cloth-bound book on production and properties of titanium metal and its alloys. It has references to the semi-technical metallurgical literature.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"Titanium and Its Compounds," by Gordon Skinner, Herrick L. Johnston, and Charles Beckett. Distributed by Herrick L. Johnston Enterprises, 540 W. Poplar St., Columbus, Ohio. An oversize, cloth-bound, lithoprinted review of the chemistry of titanium. It has an extensive bibliography, and is the best source of thermodynamic data on titanium compounds.

"Titanium," by Jelkes Barksdale (Alabama Polytechnic Institute), published by Ronald Press Co., New York, 1949. A most readable book on the chemistry of titanium compounds, but because of its early date of publication, not a good reference book on metallic titanium and its alloys. It has a very comprehensive bibliography, essentially complete from the year 1791 to July, 1949.

"Titan," Gmelin's Handbuch, System-Number 41, Verlag. Chemie, G.M.B.H., Weinheim/Bergstrasse, Germany, 1951. A definitive treatise in German covering all phases of titanium chemistry, including preparation of the metal. Only a few pages are devoted to alloys; so much information about alloys has been gained since 1951 that the Gmelin review of this aspect of titanium is already out of date.

"Titanium in Industry," by J. J. Burke, S. Abkowitz, and R. H. Hiltz, Jr. (Watertown Arsenal Laboratory), D. Van Nostrand Co. (to be published in January, 1955). Will deal with the production of titanium and titanium alloys; their physical, chemical, and mechanical properties; methods of forming, joining, welding, and fabricating into finished parts; corrosion and surface coatings; and analytical and metallographic techniques. It will review the literature through July, 1954.

Bibliographies

Besides the books listed above, all of which contain extensive bibliographies, the following independent reviews of the literature have appeared in recent years.

Battelle Memorial Institute, "Titanium Bibliography—1900 to 1951" (compiled for Watertown Arsenal Laboratory, 1952) and 1952 Supplement. Mimeographed copies of these may be obtained from the Office of Technical Services, Dept. of Commerce, Washington 25, D. C., under numbers PB No. 111196 ($3.00) and PB No. 111196S ($1.00).

"Titanium Metallurgy," a bibliography of unclassified report literature, compiled by H. E. Voress. Published by USAEC, April 14, 1953, under number TID 3039. Available from Dept. of Commerce, Office of Technical Services (55 cents). Contains 366 references to recent government reports on metallurgy.

Abstract Journals

Crerar Metals Abstracts, published by The John Crerar Library, 86 E. Randolph St., Chicago 1, Illinois. Covers current publications on titan-

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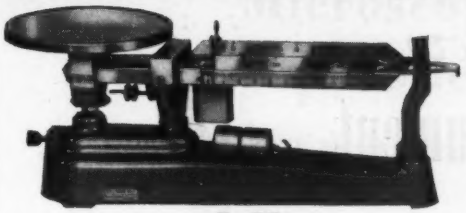

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Polaroid analyzers used in determining melting points of anisotropic crystals greatly increase accuracy of measurement, since polarization colors instantly disappear at melting point.

In practice, with or without use of polaroid elements, sample is placed between 2 round cover glasses in depression of heating block. The lid with small aperture is put in place. Temperature is raised quickly to within 10 degrees of melting point; then raised slowly until melting occurs as observed through the microscope. Thermometer is read immediately. Melting points may be obtained simultaneously on 2 or more samples or on a number of crystals from the same sample.

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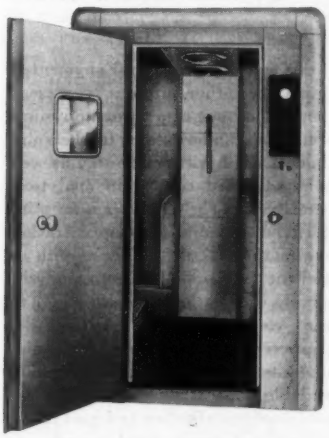
ium, zirconium, rare earths, molybdenum, and vanadium.

Chemical Abstracts, Metals Review, Battelle Technical Review, American Ceramic Society Abstracts, and other abstract journals are all good sources for the most recent literature. The *USAEC Nuclear Science Abstracts* also cover titanium.

Refrigerated Constant Temperature Rooms

A new method of balancing heating and cooling systems has permitted the design and construction of a completely new type of refrigerated constant temperature room. The Electric Hotpack Co., Inc., manufacturers of the room, have developed a method of apportioning the heated and cooled air in the constant temperature room, resulting in rapid yet close control of the conditioning medium permitting temperature control of plus or minus 1 °C. of the preset temperature.



An air-flow pattern is for heated and cooled air blended by a centrifugal circulation blower passed through diffusers in the ceiling of the room where the conditioned air is distributed uniformly throughout the interior chamber. The unique method of automatically apportioning, balancing, and blending the amounts of heated and cooled air to achieve exact and constant temperature conditions throughout the interior chamber, has permitted the construction of a unit with loading capacities up to 210 cu. ft. that will maintain the control accuracy found in small "research" laboratory ovens.

The rooms are for operation from 5° to 40 °C. and are made in a variety of sizes up to 210 cu. ft. capacity.

Further information is available from Electric Hotpack Co., Inc., Cottman Ave. at Melrose St., Philadelphia 35, Pennsylvania.

New Chemicals

● Bios Laboratories, Inc., 17 W. 60th St., New York 23, New York, announces the availability of the following new chemicals: Chlorogenic Acid, $C_{16}H_{18}O_9$, m. w. 354.3; Dehydroascorbic Acid, $C_6H_6O_6$, m. w. 174.1; Diacetoneglucose, $C_{12}H_{20}O_6$, m. w. 260.3; 1,2,5,6-Dibenzanthracene, $C_{22}H_{14}$, m. w. 278.3; 6,7-Dichlororibo-

NOW Polarized Light Microscopy with a Stereoscopic Microscope

Ingenious new device by AO permits right-side-up images under polarized light

The new AO No. 507 Polarizing Attachment for Stereoscopic Microscopes, developed at the suggestion of petroleum geologists, will doubtless have many applications in other fields concerned with sedimentation studies. Easily attached to AO Spencer Stereoscopic Microscopes Nos. 25 and 28, it provides *erect* three-dimensional images under *polarized* light.

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Simply substitute this polarizing attachment for the usual glass plate stage of the microscope. The polarizer, recessed in the attachment's stage proper, can't fall out, can't shift out of position. The No. 507's rotating circular metal stage, graduated in 5 degree intervals for gross quantitative work, is easily centered in the optical system by three thumb screws.

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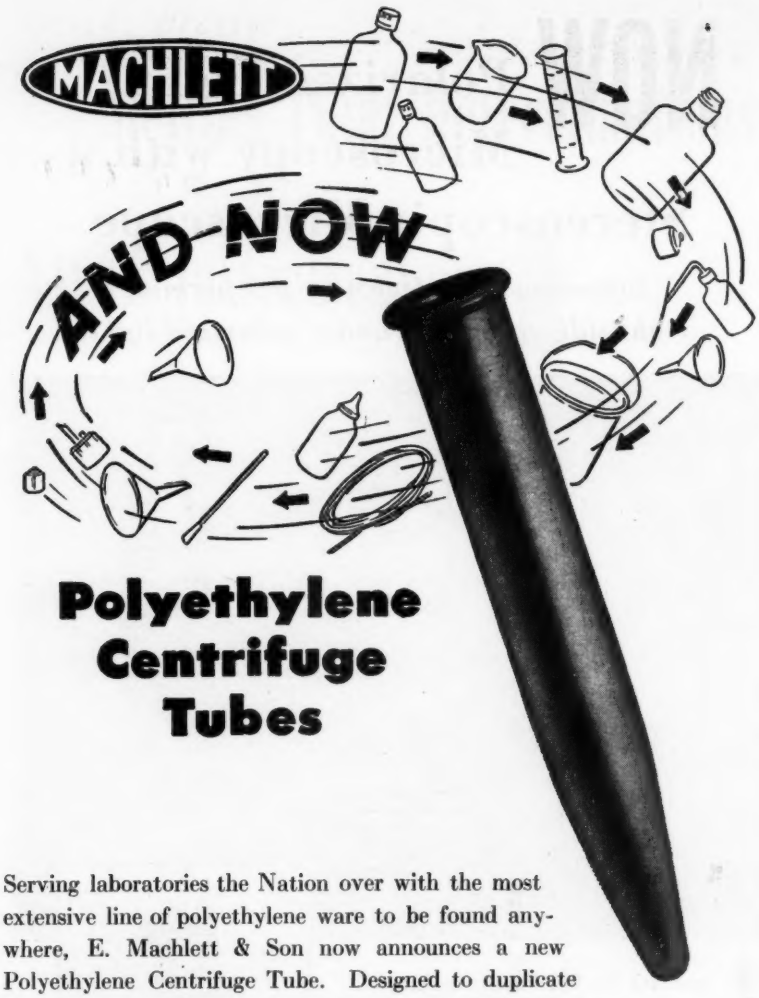

Polyethylene Centrifuge Tubes

Serving laboratories the Nation over with the most extensive line of polyethylene ware to be found anywhere, E. Machlett & Son now announces a new Polyethylene Centrifuge Tube. Designed to duplicate their glass counterparts, these tubes offer all of the advantages associated with polyethylene ware.

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Associate Professor of Physiology, State University of New York Medical Center at Syracuse, Syracuse, N. Y.

In this second revised and augmented edition, the author purposes "to present a simple account of polarography in a form which can be used by teachers and students in physical chemistry as well as in advanced courses in analytical chemistry." The emphasis is on principles and the scope is descriptive rather than mathematical. It begins with an excellent review of electroanalysis, showing the relation of polarography to other electro methods. A brief description of apparatus includes equipment constructible from parts readily available in many laboratories. Fundamentals of quantitative and qualitative analysis and recent developments are discussed in some detail. Chapters on applications and suggestions for practical polarography complete the book.

A particularly good feature is the inclusion of 26 experiments, and the graphs and tables of data obtained from them constitute the illustrative material of the text. These experiments could be undertaken with profit by anyone desiring an experimental indoctrination in polarography.

The book is especially recommended to students, beginners in the field, and anyone desiring a brief but comprehensive introduction of the fundamentals of polarographic measurements.

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● Three specifically labeled carbohydrates have been added to the list of radioactive carbon compounds available from the Nuclear Instrument and Chemical Corp., 229 W. Erie St., Chicago 10, Illinois. They will be especially useful to workers in the fields of nutrition, intermediary metabolism, fermentation, and photosynthesis.

These materials, made available for the first time to research workers, are D-Glucose-1-C-14, D-Glucono-*delta*-lactone-1-C-14, and D-Mannose-1-C-14. They are available in four package sizes from 1 to 0.05 millicurie under regular A.E.C. licensing procedures.

A complete list of over 100 radioactive carbon compounds available from Nuclear-Chicago may be obtained on request.

● A new service of Mann Research Laboratories, 136 Liberty St., New York 6, New York, is announced with their series of kits containing biochemical substances which may be used in conjunction with one another in certain fields of scientific research.

The first in this series is the "Mann Protease Substrate Kit" containing 9 substrates specific for the determination and characterization of 9 different protcolytic enzyme systems.

Enzyme System	*Substrate*
Aminopolypeptidase	Leucylglycylglycine
Carboxypeptidase	CBZ-glycyl-L-phenylalanine
Chymotrypsin	CBZ-glycyl-L-phenylalanine amide
Dipeptidase	Glycylglycine
Ficin	Benzoylglycine amide
Leucylpeptidase	Leucylglycine
Papain	Benzoylarginine amide and Cysteine Hydrochloride as activator
Pepsin	CBZ-L-glutamyl-L-tyrosine
Trypsin	Benzoylarginine Methylester Hydrochloride

Included with the kit is a list of pertinent references and other information which the research worker will find useful.

New Microspectrophotometer Analyses Both Micro and Macro Samples

A new double beam microspectrophotometer that can be used to analyze solutions in volumes ranging from as small as 0.015 ml. up to several milliliters has just been announced by the Jarrell-Ash Company. The versatility of the new instrument is the result of a unique design feature that allows the use of interchangeable micro and macro cuvettes of the appropriate volume and path length. No other change of components or settings is necessary when switching from one sample to another.

The new instrument utilizes a single meter that is calibrated to indicate the ratio of the optical densities of concentrations. This simplified system produces readings that are linear with concentration, reduces the lapsed time per sample to approximately 30 seconds and makes possible time reaction studies.

Both ultraviolet and visible light sources are provided with the instrument and they are instantly interchangeable by merely turning a panel switch. Spectral range covers the area from approximately 210 to over 600 millimicrons/mm. and monochromator dispersion is 4.4 millimicrons/-mm.

More information on the JAco Microspectrophotometer, including a descriptive bulletin sheet, is available by writing Mr. Richard Ashley, Jarrell-Ash Co., 26 Farwell St., Newtonville, Massachusetts.

New Literature

● Bulletin 50, a 4-page, 2-color brochure describing the new Inducto line of high frequency induction melting and heating equipment has been issued by the Inductotherm Corp., 620 E. Glenolden Ave., Glenolden, Pennsylvania. The bulletin describes a new laboratory unit, the Inducto Melting, a unique piece of equipment in which the melting table is integral with the control cabinet and power supply. Featured in the bulletin are two melting charts which simplify the selection of the proper size unit. Bulletins are available upon request from Inductotherm Corp., Glenolden, Pennsylvania.

● A 4-page bulletin on phenylfluorone, a reagent for determining germanium colorimetrically, is now available from Jasonols Chemical Corp., 825 E. 42 St., Brooklyn 10, New York.

● A Magnetic Energy Spectrum Chart is included in the new 8-page "Palo Retort". It describes for the first time a number of new laboratory items. Copies may be secured upon request, by writing to Palo Laboratory Supplies, Inc., 81 Reade St., New York 7, N. Y.

● A catalogue describing its complete line of Diffusion Pumps is available from Naresco Equipment Corp., equipment sales subsidiary of National Research Cor-

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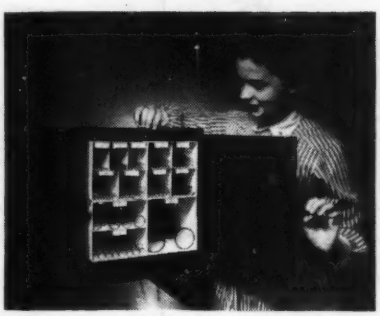

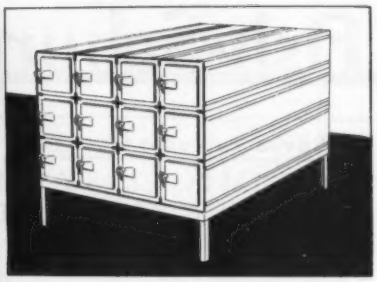

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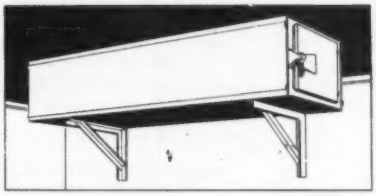

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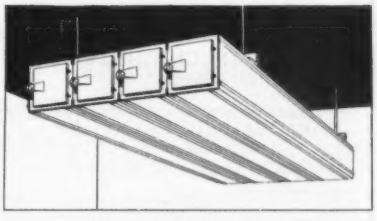

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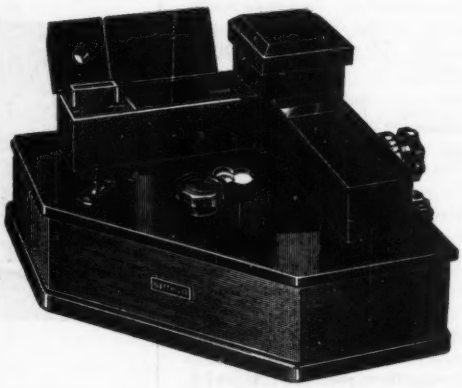

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poration, 160 Charlemont St., Newton Highlands, 61, Massachusetts. This catalogue gives the characteristics of each pump, including pumping speeds, operating pressures, blank-off pressures, and forepressure limits.

● A completely new line of pressure measuring elements with greater operating power and improved accuracy are described in Bulletin 6-10, "Pressure Recorders," just issued by The Foxboro Co., Foxboro, Massachusetts. This 24-page publication contains an application chart "How to Select the Measuring Element," which shows the wide choice of element materials available, such as corrosion resistant Type 316 stainless steel, beryllium copper, and Ni-Span which is unaffected by ambient temperatures. The exclusive Foxboro high-pressure helical for pressures to 80,000 p. s. i., as well as the diaphragm, bellows, spiral and standard helical covering ranges from 10 inches of water to 6000 p. s. i., are diagramed and explained. Exact ranges are listed for each material and each type of element.

● The new 24-page catalogue on Chromatography, including a full and authoritative documentation with references, is now available from Will Corp., Rochester 3, New York. This catalogue describes the latest in equipment, apparatus, and supplies, including solvents and adsorbents, preferred by workers in the field of chromatography.

● Photovolt Corp., 95 Madison Ave., New York, New York now has available, a new edition of their Bulletin No. 100 describing their line of photoelectric and electronic measuring instruments. Of special interest is the newly developed Densitometer for Paper Electrophoresis and Chromatography. Copies available on request.

● Bulletin No. 307, now available from Burrell Corp., offers information on a new line of Burrell Wrist-Action Shakers.

The new bulletin pictures and describes all build-up combinations available and offers three different types of flask holders. Charts list catalogue numbers and prices for ease of ordering as well as container sizes and capacities which may be employed.

● The Atomic Industrial Forum, Inc., announces publication of its report on "Nuclear Reactor Development." This report is the proceedings of a meeting in Washington on May 24, 1954, during which the top men in reactor development covered the A. E. C.'s five-year reactor program as well as private industrial developments in the field. The speakers gave up-to-date summaries on major programs now under way, outlined their plans for the future, and answered pertinent questions from the floor. Every major effort in the country on reactor development was represented on the program.

This is the first time that the complete story on nuclear power in the United States has become available in a single report. Not only is the report the most complete summary published to date, but its technical level will make it of interest to both management and research people.

The report is available at $5.00 per copy from the Atomic Industrial Forum, Inc., 260 Madison Ave., New York 16, New York.

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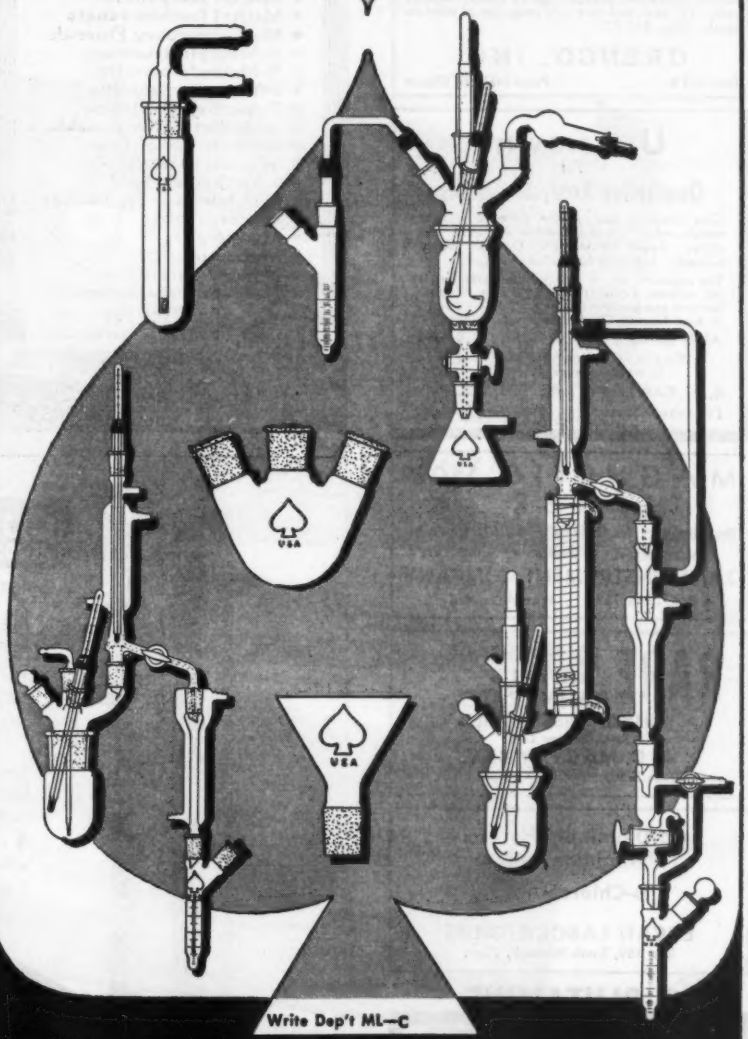

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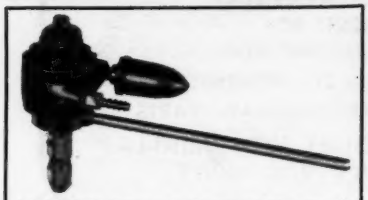

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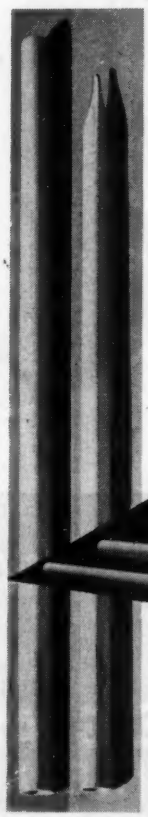

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